Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

A 4-ethylpyridine complex of tetrachloromolybdenum(III) and its oxidation product

Barbara Modec,* Jurij V. Brenčič and Ljubo Golič

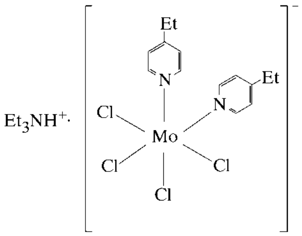
Faculty of Chemistry and Chemical Technology, University of Ljubljana,
Aškerčeva 5, PO Box 537, 1000 Ljubljana, Slovenia
Correspondence e-mail: barbara.modec@guest.arnes.si

Received 22 March 2000
Accepted 5 April 2000

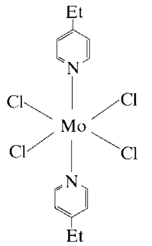
The Mo atoms in the title compounds, *i.e.* triethylammonium *cis*-tetrachlorobis(4-ethylpyridine-*N*)molybdate(III), *cis*-$(C_6H_{16}N)[MoCl_4(C_7H_9N)_2]$, and *trans*-tetrachlorobis(4-ethylpyridine-*N*)molybdenum(IV), *trans*-$[MoCl_4(C_7H_9N)_2]$, are six-coordinate with octahedral geometry. The Mo atom in the latter complex lies on a site with crystallographic 2/*m* symmetry.

Comment

$[MoX_6]^{3-}$ (X = Cl^- or Br^-) reacts with pyridine to give various halopyridine complexes, *e.g.* $[MoX_5(py)]^{2-}$ (py = pyridine, C_5H_5N; Modec *et al.*, 1998), *trans*- and *cis*-$[MoX_4(py)_2]^-$ (Brenčič *et al.*, 1993, 1994), *mer*-$[MoX_3(py)_3]$ (Brenčič, 1974) and *trans*-$[MoX_2(py)_4]^+$ (Brenčič *et al.*, 1996). On partial substitution of the chloro ligands in $[MoCl_6]^{3-}$ with 4-ethylpyridine (4-Etpy), both *trans* and *cis* geometric isomers of $[MoCl_4(4\text{-}Etpy)_2]^-$ were obtained. Bromine oxidation of both resulted in a molybdenum(IV) complex with a *trans* configuration of 4-ethylpyridine ligands, suggesting a rearrangement of ligands during the electron transfer. We report here the structures of triethylammonium *cis*-tetrachlorobis-(4-ethylpyridine-*N*)molybdate(III), (I), and *trans*-tetrachlorobis(4-ethylpyridine-*N*)molybdenum(IV), (II).



(I)



(II)

While many tetrahalobispyridinemetalates(III) with a *trans* configuration of ligands are known, there are only a few structurally characterized *cis* isomers, namely *cis*-NH_4-$[MoCl_4(py)_2]\cdot py\cdot H_2O$ (Leban *et al.*, 1994), *cis*-$NH_4[MoBr_4(py)_2]\cdot\frac{1}{3}H_2O$ (Brenčič *et al.*, 1994) and *cis*-$(Et_4N)[OsCl_4(py)_2]$ (Kolf & Preetz, 1999). Also $(PPh_4)[MoCl_4(bipy)]$ (Richards *et al.*, 1987), with the bidentate N-donor ligand 2,2′-bipyridine (bipy), displays a similar geometry, with the two N atoms in a *cis* arrangement. Selected bond lengths and angles for (I) (Fig. 1) are given in Table 1. Four Cl atoms at distances in the range 2.423 (1)–2.438 (1) Å and two N atoms at distances of 2.196 (2) and 2.206 (4) Å make up the octahedral coordination of the Mo atom. These distances are comparable to those found in related compounds, for example, in *cis*-NH_4-$[MoCl_4(py)_2]\cdot py\cdot H_2O$ [Mo—Cl 2.423 (2)–2.446 (2) Å and Mo—N 2.202 (5) and 2.206 (4) Å; Leban *et al.*, 1994]. Because of the orientation of the aromatic rings, the *cis*-$[MoCl_4(4\text{-}Etpy)_2]^-$ complex anion possesses no symmetry element. The dihedral angle between the planes of the two pyridine ligands is 49.8 (2)°. Compound (I) crystallizes in an non-centrosymmetric space group, $Pca2_1$, while other *cis* compounds crystallize as racemic mixtures in centrosymmetric space groups. The N3 atom of the triethylammonium cation is linked *via* two hydrogen bonds with chlorines from the coordination anion [N3···Cl3 3.482 (4) Å and N3···Cl4 3.449 (4) Å]. High thermal motion was observed for the ethyl C atoms of the 4-ethylpyridine ligand and in the case of C27, a possible disorder over two positions was suggested.

Among the compounds $[ZrCl_4(py)_2]$ (CSD refcode FUFSOO; Troyanov, 1987), $[TiCl_4(py)_2]$ (GAMGAC; Mazo *et al.*, 1987), $[TaCl_4(py)_2]$ (LATVUX; Miller *et al.*, 1993), $[PtCl_4(py)_2]$ (TULFIP; Junicke *et al.*, 1997) and $[WCl_4(py)_2]$ (CPYRDW10; Brenčič *et al.*, 1979) [Cambridge Structural Database (CSD), October 1999 release; Allen & Kennard, 1993], not only are they all *trans* isomers, but their structures are isotypic, as shown by a comparison of the unit-cell dimensions. $[M^{IV}Cl_4(py)_2]$ has a C_{2h} site-group symmetry. The ethyl groups on pyridine in (II) (Fig. 2) affect the unit-cell dimensions, leaving the overall symmetry of the complex intact. The Mo atom occupies a 2/*m* special position. The 4-ethylpyridine

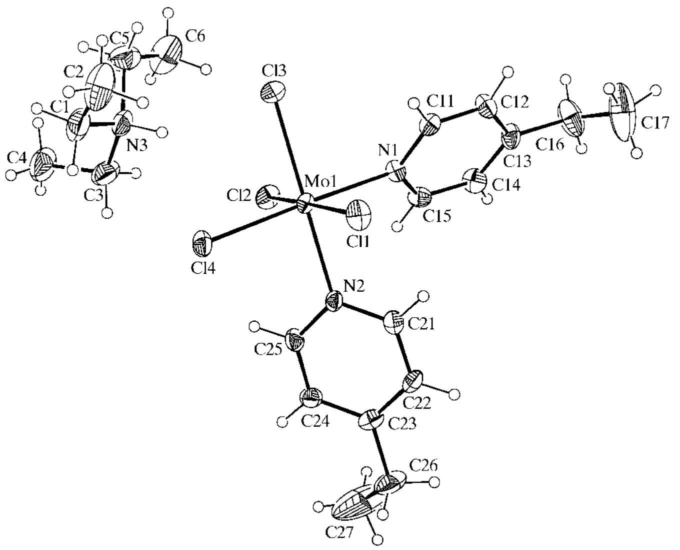


Figure 1
The structure of (I) with displacement ellipsoids drawn at the 30% probability level. H atoms are of arbitrary size.

rings, which lie on a mirror plane, are in an eclipsed conformation. Four Cl atoms are bonded to molybdenum at distances of 2.340 (1) Å and two N atoms are bonded at distances of 2.195 (3) Å (Table 3).

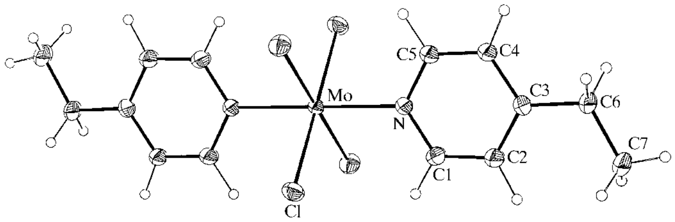


Figure 2
The molecular structure of (II), showing the atom-numbering scheme and 30% probability displacement ellipsoids. H atoms are of arbitrary size.

Experimental

To a solution of *cis*-*L*H$[MoCl_4L_2]$ (*L* = 4-ethylpyridine; 150 mg, 0.268 mmol) in acetonitrile (15 ml), triethylamine (5 ml) and ether (50 ml) were added. The solution was left to stand overnight in an ice bath. Crystals of (I) were obtained in 35% yield (52 mg). Analysis calculated (found) in %: C 43.34 (43.38), H 6.18 (6.31), N 7.58 (7.40). IR data (nujol, cm^{-1}): 3091 (*m*), 1617 (*vvs*), 1550 (*w*), 1315 (*w*), 1285 (*w*), 1224 (*m*), 1207 (*w*), 1180 (*w*), 1172 (*w*), 1153 (*w*), 1083 (*w*), 1065 (*m*), 1054 (*w*), 1028 (*vs*), 1009 (*w*), 976 (*w*), 845 (*vvs*), 789 (*m*), 722 (*m*), 667 (*w*), 578 (*m*), 512 (*m*), 304 (*vvs*), 284 (*s*), 272 (*sh*). For the preparation of (II), a solution of *trans*-*L*H$[MoCl_4L_2]$ (*L* = 4-ethylpyridine; 30 mg, 0.0535 mmol) in nitromethane (5 ml) and acetonitrile (5 ml) was placed in a chamber containing bromine fumes. Within a few hours, red crystals of (II) had grown from the solution. Analysis calculated (found) in %: C 37.20 (36.92), H 4.01 (3.90), N 6.20 (6.29). IR data (nujol, cm^{-1}): 1618 (*vs*), 1549 (*w*), 1500 (*m*), 1308 (*m*), 1222 (*m*), 1193 (*w*), 1063 (*vs*), 1054 (*m*), 1030 (*vs*), 979 (*w*), 957 (*w*), 833 (*vvs*), 792 (*m*), 780 (*w*), 767 (*w*), 721 (*m*), 702 (*w*), 669 (*w*), 561 (*w*), 497 (*s*), 430 (*w*).

Compound (I)

Crystal data

$(C_6H_{16}N)[MoCl_4(C_7H_9N)_2]$
$M_r = 554.24$
Orthorhombic, $Pca2_1$
$a = 19.7025$ (9) Å
$b = 7.766$ (2) Å
$c = 16.7929$ (6) Å
$V = 2569.6$ (6) Å^3
$Z = 4$
$D_x = 1.433$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 12 687 reflections
$\theta = 3.75$–$25.02°$
$\mu = 0.937$ mm^{-1}
$T = 293$ (2) K
Prism, yellow
0.50 × 0.30 × 0.15 mm

Data collection

Quantum CCD Rigaku AFC-7 diffractometer
φ and ω scans
Absorption correction: empirical (*REQABA*; Jacobson, 1997)
$T_{min} = 0.739$, $T_{max} = 0.869$
18 043 measured reflections
5860 independent reflections
3267 reflections with $I > 2\sigma(I)$
$R_{int} = 0.041$
$\theta_{max} = 26.37°$
$h = 0 \rightarrow 23$
$k = -8 \rightarrow 8$
$l = -19 \rightarrow 19$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.059$
$S = 1.027$
4069 reflections
253 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0285P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.81$ e Å^{-3}
$\Delta\rho_{min} = -0.49$ e Å^{-3}
Absolute structure: Flack (1983); 1518 Friedel pairs
Flack parameter = −0.03 (4)

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

Mo1—N1	2.196 (2)	Mo1—Cl3	2.431 (1)
Mo1—N2	2.206 (4)	Mo1—Cl2	2.436 (1)
Mo1—Cl1	2.423 (1)	Mo1—Cl4	2.438 (1)
N1—Mo1—N2	89.0 (1)	Cl1—Mo1—Cl2	173.16 (5)
N1—Mo1—Cl1	87.55 (9)	Cl3—Mo1—Cl2	90.84 (5)
N2—Mo1—Cl1	87.8 (1)	N1—Mo1—Cl4	177.83 (9)
N1—Mo1—Cl3	90.4 (1)	N2—Mo1—Cl4	89.0 (1)
N2—Mo1—Cl3	178.5 (1)	Cl1—Mo1—Cl4	93.11 (5)
Cl1—Mo1—Cl3	93.59 (4)	Cl3—Mo1—Cl4	91.66 (5)
N1—Mo1—Cl2	87.20 (9)	Cl2—Mo1—Cl4	91.98 (5)
N2—Mo1—Cl2	87.8 (1)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3···Cl3	0.91	2.67	3.482 (4)	149
N3—H3···Cl4	0.91	2.83	3.449 (4)	127

Compound (II)

Crystal data

$[MoCl_4(C_7H_9N)_2]$
$M_r = 452.06$
Monoclinic, $C2/m$
$a = 16.1077$ (8) Å
$b = 7.6691$ (4) Å
$c = 7.1566$ (4) Å
$\beta = 98.012$ (4)°
$V = 875.44$ (8) Å^3
$Z = 2$
$D_x = 1.715$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 50 reflections
$\theta = 10.04$–$20.10°$
$\mu = 1.35$ mm^{-1}
$T = 293$ K
Prism, red
0.19 × 0.11 × 0.10 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
5116 measured reflections
1358 independent reflections
1114 reflections with $I > 3\sigma(I)$
$R_{int} = 0.015$
$\theta_{max} = 29.95°$
$h = -22 \rightarrow 22$
$k = -10 \rightarrow 10$
$l = -10 \rightarrow 10$
3 standard reflections every 300 reflections intensity decay: 0.61%

Refinement

Refinement on F
$R = 0.017$
$wR = 0.028$
$S = 1.005$
1114 reflections
62 parameters
H-atom parameters not refined
$(\Delta/\sigma)_{max} = 0.001$
$w = W_F{\cdot}W_S$, where $W_F(F_o < 20) = (F_o/20)^{1.5}$, $W_F(F_o > 22) = (22/F_o)^1$, $W_F(20 < F_o < 22) = 1$, and $W_S(\sin\Theta < 0.48) = (0.48/\sin\Theta)^{2.0}$, $W_S(\sin\Theta > 0.56) = (\sin\Theta/0.56)^{2.0}$, $W_S(0.48 < \sin\Theta < 0.56) = 1$
$\Delta\rho_{max} = 0.54$ e Å^{-3}
$\Delta\rho_{min} = -0.53$ e Å^{-3}

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

Mo—Cl	2.340 (1)	Mo—N	2.195 (3)
Cl—Mo—N	90.27 (8)	Cl—Mo—N^{i}	89.73 (8)
Cl—Mo—Cl^{i}	90.31 (3)	Cl—Mo—Cl^{ii}	89.69 (3)

Symmetry codes: (i) $1 - x, y, 1 - z$; (ii) $x, 1 - y, z$.

For compound (I), data collection: *d*trek* (Molecular Structure Corporation, 1997); cell refinement: *d*trek*; data reduction: *d*trek*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*III (Burnett & Johnson, 1996). For compound (II), data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *Xtal*3.4 *DIFDAT, SORTRF* and *ADDREF* (Hall *et al.*, 1995); program(s) used to solve structure: *Xtal*3.4; program(s) used to refine structure: *Xtal*3.4 *CRYLSQ*; molecular graphics: *ORTEP*III (Burnett & Johnson, 1996); software used to prepare material for publication: *Xtal*3.4 *BONDLA* and *CIFIO*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1469). Services for accessing these data are described at the back of the journal.

References

Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 31–37.
Brenčič, J. V. (1974). *Z. Anorg. Allg. Chem.* **403**, 218–224.
Brenčič, J. V., Čeh, B., Leban, I., Modec, B. & Rotar, R. (1993). *Z. Anorg. Allg. Chem.* **619**, 796–800.
Brenčič, J. V., Čeh, B. & Segedin, P. (1979). *Z. Anorg. Allg. Chem.* **454**, 181–186.
Brenčič, J. V., Golič, L., Leban, I., Rotar, R. & Sieler, J. (1996). *Z. Anorg. Allg. Chem.* **622**, 2124–2128.
Brenčič, J. V., Leban, I. & Modec, B. (1994). *Z. Anorg. Allg. Chem.* **620**, 950–954.
Burnett, M. N. & Johnson, C. K. (1996). *ORTEP*III. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.
Enraf–Nonius (1989). *CAD*-4 *Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Hall, S. R., King, G. S. D. & Stewart, J. M. (1995). Editors. *Xtal*3.4 *User's Manual*. University of Western Australia, Australia.
Jacobson, R. A. (1997). *REQABA*. Ames Laboratory, Iowa State University, USA.
Junicke, H., Schenzel, K., Heinemann, F. W., Pelz, K., Bögel, H. & Steinborn, D. (1997). *Z. Anorg. Allg. Chem.* **623**, 603–607.
Kolf, S. & Preetz, W. (1999). *Z. Anorg. Allg. Chem.* **625**, 411–416.
Leban, I., Modec, B. & Brenčič, J. V. (1994). *Acta Cryst.* C**50**, 1546–1548.
Mazo, F. N., Bobilev, A. P. & Troyanov, S. I. (1987). *Vestn. Mosk. Univ. Ser. Khim.* **28**, 459.
Miller, G. J., Lin, J. & Young, V. Jr (1993). *Acta Cryst.* C**49**, 1770–1773.
Modec, B., Papoular, R. & Brenčič, J. V. (1998). *Acta Cryst.* C**54**, 736–738.
Molecular Structure Corporation (1997). *d*trek*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Richards, R. L., Shortman, C., Povey, D. C. & Smith, G. W. (1987). *Acta Cryst.* C**43**, 2091–2093.
Sheldrick, G. M. (1997). *SHELXL*97 and *SHELXS*97. University of Göttingen, Germany.
Troyanov, S. I. (1987). *Koord. Chem.* **13**, 1123–1125.