Dioxodichlorodiaquamolybdenum(VI)–Bis(pyridinium chloride)

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Abstract. $C_{10}H_{16}Cl_4MoN_2O_4$, monoclinic, $C2/c$, $a = 10\cdot193$ (4), $b = 33\cdot618$ (10), $c = 6\cdot650$ (2) Å, $\beta = 127\cdot95$ (2)°, $Z = 4$, $D_o = 1\cdot67$, $D_x = 1\cdot722$ g cm^{-3}. Final $R = 0\cdot046$. The crystal contains neutral $MoO_2Cl_2(H_2O)_2$ molecules, pyridinium and Cl$^-$ ions. The Mo atom is octahedrally coordinated by two oxo O atoms at $1\cdot701$ Å, two water O atoms at $2\cdot268$ Å, and two Cl atoms at $2\cdot356$ Å. The two oxo O atoms are *cis* to each other.

Introduction. The crystals were prepared as described in the literature (Weinland & Knöll, 1905). From Weissenberg photographs and the systematic absences for hkl, $h+k$ odd, $h0l$, l odd and $0k0$, k odd the permissible space groups were Cc and $C2/c$. The group $C2/c$ was chosen because there was no significant improvement in R from the use of Cc and because of the unsatisfactory bond lengths and angles in Cc. A crystal $0\cdot11 \times 0\cdot11 \times 0\cdot20$ mm was used to measure the lattice parameters and intensities. The cell constants were determined by least-squares analysis of the angular settings of 22 reflexions ($\lambda = 1\cdot5418$ Å). The intensities of 1516 independent reflexions [1437 reflexions had $I \geq 3\sigma(I)$ and were regarded as observed; three reflexions which appeared to show extinction were removed] with $2\theta < 60°$ were measured on a Philips PW1100 automated diffractometer by the ω–2θ scan technique (scan speed $0\cdot04°$ s^{-1}, scan range $1\cdot2°$) with Cu $K\alpha$ radiation and a graphite monochromator. Lorentz and polarization corrections were applied but no absorption correction was made ($\mu = 68\cdot9$ cm^{-1}). The structure was solved by the heavy-atom technique and refined by full-matrix least squares to $R = 0\cdot046$ (corresponding $R' = 0\cdot051$) for 1434 reflexions.* The function minimized was $\sum w(|F_o| - |F_c|)^2$, where w was defined as $1/\sigma^2(F_o)$. The scattering factors for all atoms were taken from *International Tables for X-ray Crystallography* (1962) with corrections for anomalous scattering for the Mo and Cl atoms according to Cromer & Liberman (1970). The atomic coordinates of non-H atoms are listed in Table 1, and the interatomic distances and angles in Table 2.

Discussion. Anhydrous MoO_2Cl_2 has a layer structure in which both oxo O atoms participate in the Mo–O–Mo bridging system (Atovmyan, Aliev & Tarakanov, 1968). In the monohydrate, $MoO_2Cl_2.H_2O$, the entering of a water molecule into the coordination sphere of Mo atoms breaks down the layers into chains in which one oxo O atom is bridging and one is terminal (Atovmyan & Aliev, 1971; Schröder & Christensen, 1972). When two water molecules are coordinated to the Mo atom, the structure consists of isolated $MoO_2Cl_2(H_2O)_2$ molecules as shown in the

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Table 1. *Final positional and thermal parameters* ($\times 10^4$)

The anisotropic temperature factor is exp $[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + 2b_{12}hk + 2b_{13}hl + 2b_{23}kl)]$. Standard deviations in units of the last significant digits are given in parentheses.

	x	y	z	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Mo	0	808 (0)	$\frac{1}{4}$	123 (1)	6 (0)	320 (3)	0	262 (3)	0
Cl(1)	2862 (2)	956 (0)	5234 (3)	109 (2)	12 (0)	315 (6)	12 (1)	235 (6)	14 (1)
Cl(2)	2626 (2)	1665 (0)	−57 (3)	154 (3)	12 (0)	304 (6)	−21 (1)	288 (6)	−12 (1)
O(1)	12 (7)	493 (2)	509 (12)	214 (10)	14 (1)	739 (31)	−6 (4)	438 (31)	−112 (7)
O(2)$_w$	21 (5)	1333 (1)	382 (8)	134 (7)	14 (1)	296 (16)	2 (3)	257 (18)	47 (4)
C(11)	$\frac{1}{2}$	41 (3)	$\frac{1}{4}$	295 (24)	8 (1)	495 (43)	0	634 (59)	0
C(12)	6476 (10)	243 (2)	4057 (14)	235 (16)	14 (1)	430 (30)	17 (6)	479 (39)	16 (8)
C(13)	6431 (11)	654 (3)	4023 (15)	307 (21)	15 (1)	486 (35)	−52 (7)	678 (49)	−61 (9)
C(14)	$\frac{1}{2}$	836 (2)	$\frac{1}{4}$	324 (26)	6 (1)	597 (48)	0	846 (67)	0
C(21)	0	2244 (3)	$\frac{1}{4}$	459 (47)	7 (1)	1608 (158)	0	1292 (153)	0
C(22)	508 (14)	2444 (3)	4616 (23)	312 (24)	17 (1)	897 (64)	55 (9)	785 (69)	104 (14)
C(23)	516 (10)	2837 (3)	4673 (16)	205 (15)	15 (1)	530 (36)	8 (6)	427 (40)	−39 (9)
C(24)	0	3044 (3)	$\frac{1}{4}$	232 (24)	8 (1)	1070 (94)	0	654 (81)	0

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Table 2. *Interatomic distances* (Å) *and angles* (°)

The estimated standard deviations are in parentheses. Primed atoms are related to the corresponding unprimed atoms by the twofold axis. Superscripts refer to atoms in the following positions: (i) $x,y,-\frac{1}{2}+z$; (ii) $\frac{1}{2}+x,\frac{1}{2}-y,\frac{1}{2}-z$.

Mo —O(1)	1·701 (8)	Cl(1)—Mo —O(1)	97·7 (2)
Mo —O(2)$_w$	2·268 (5)	Cl(1)—Mo —O(2)	80·5 (1)
Mo —Cl(1)	2·356 (1)	Cl(1)—Mo —Cl(1')	155·5 (1)
		O(1)—Mo —O(2)$_w$	89·7 (3)
C(11)–C(12)	1·373 (9)	O(1)—Mo —O(1')	103·0 (5)
C(12)–C(13)	1·382 (12)	O(1)—Mo —O(2')$_w$	167·3 (4)
C(13)–C(14)	1·309 (9)	O(2)$_w$–Mo —O(2')$_w$	77·8 (4)
C(21)–C(22)	1·343 (15)	C(12')–C(11)–C(12)	120·6 (6)
C(22)–C(23)	1·321 (14)	C(11)–C(12)–C(13)	118·3 (7)
C(23)–C(24)	1·384 (12)	C(12)–C(13)–C(14)	119·3 (7)
		C(13)–C(14)–C(13')	124·3 (6)
O(1)····O(1')	2·662 (6)		
O(2)$_w$····O(2')$_w$	2·844 (5)	C(22')–C(21)–C(22)	120·1 (8)
O(1)····O(2)$_w$	2·826 (7)	C(21)–C(22)–C(23)	121·4 (12)
		C(22)–C(23)–C(24)	118·7 (11)
O(2)$_w$····Cl(2)	3·056 (8)	C(23)–C(24)–C(23')	121·6 (9)
O(2^i)$_w$···Cl(2)	3·054 (8)		
C(23^{ii})···Cl(2)	3·299 (8)		
C(14)····Cl(2)	3·382 (8)		

Fig. 1. Clinographic projection of the structure of $MoO_2Cl_2(H_2O)_2.2C_5H_5NHCl$ and the atomic numbering. Primed atoms are related to the corresponding unprimed atoms by a twofold symmetry axis.

present structure analysis.* As shown in Fig. 1 the structure of $MoO_2Cl_2(H_2O)_2.2C_5H_5NHCl$ is built up from the neutral Mo complex, pyridinium and Cl⁻ ions. The $MoO_2Cl_2(H_2O)_2$ complex molecules and the Cl⁻ ions are linked together in the structure along c through O(2)$_w$···Cl(2) and O(2^i)$_w$···Cl(2) hydrogen bonds of 3·056 and 3·054 Å respectively. The closest contact distances between pyridinium and Cl⁻ ions are C(23^{ii})···Cl(2) 3·299 and C(14)···Cl(2) 3·382 Å. The Mo complex as well as the pyridinium cations have crystallographically imposed twofold symmetry axes. The Mo atom has distorted octahedral coordination, being bonded to two oxo O atoms at 1·701 Å, two water O atoms at 2·268 Å and to two Cl atoms at 2·356 Å. The oxo O atoms are in cis-positions with the O(1)–Mo–O(1') angle 103·0°. The Mo–oxo O bond length and the angle within the cis-MoO₂ group are in agreement with the corresponding values reported for numerous dioxomolybdenum complexes (see for example Kamenar, Penavić & Prout, 1973; Tsukuma, Kawaguchi & Watanabé, 1975; Schröder, 1975). The Mo–OH₂ and Mo–Cl bond lengths can also be compared with the corresponding values found in other complexes containing such bonds; in $K[MoO_2Cl_2(H_2O)]_3Cl$ the Mo–OH₂ bond length is 2·25 Å and the Mo –Cl bond length 2·38 Å (Atovmyan & Krasochka, 1971), while in $MoO_2Cl_2.H_2O$ these bond lengths are 2·301 and 2·352 Å respectively (Schröder & Christensen, 1972).

We were not able to distinguish the N from the C atoms within the pyridinium rings; thus all atoms in

the rings were treated as C atoms. A comparison of the dimensions of the pyridinium ions in the present structure with the pyridinium ion in the structure of pyridine hydrochloride (Rérat, 1962) gives the possibility for the atom C(14) in the ring C(11)–C(14) to be considered as N. For the ring C(21)–C(24) there is no such indication for the N atom position. The environment of the pyridinium cations does not give any information either as to the most probable position of the N atoms. Relatively high temperature factors of the ring atoms may indicate some disordering in the atomic positions.

* Note added in proof: -The structure of the analogous complex $MoO_2Cl_2(H_2O)_2.2KCl$ has been reported in the monograph: Poray-Koshits, M. A. & Atovmyan, L. O. (1974). *Kristallokhimiya i Stereokhimiya Koordinacionnykh Soedinenii Molibdena*, p. 125. Moscow: Izd. Nauka.
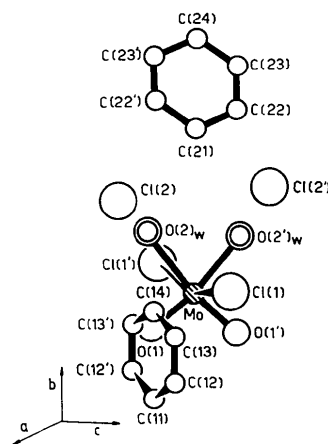
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