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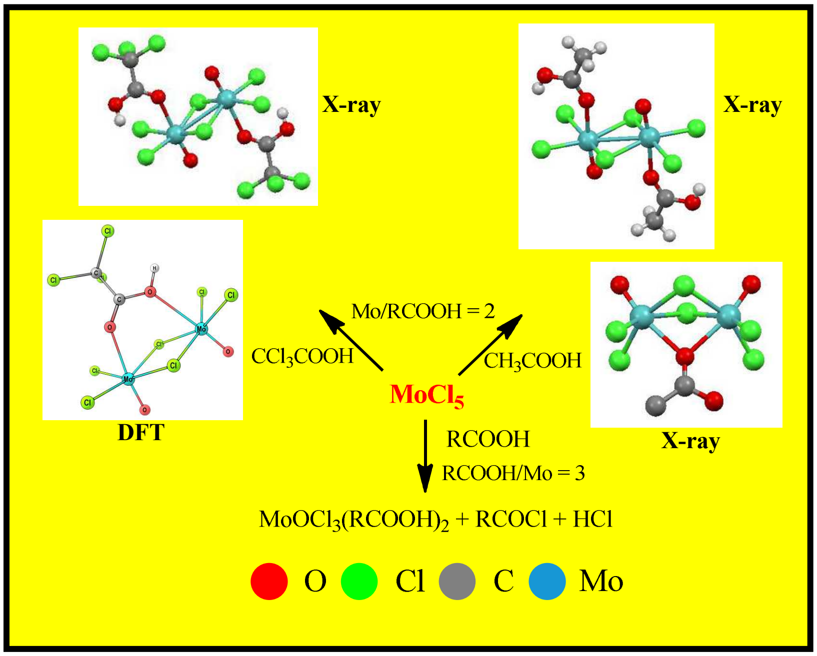
Graphical Abstract

The reactivity of $MoCl_5$ with carboxylic acids has been elucidated for the first time. The reactions are featured by the chlorinating behaviour of $MoCl_5$, rather than affording the respective carboxylato complexes.

Synopsis Artwork



Oxido-Molybdenum Complexes Obtained by Cl/O Interchange Between MoCl$_5$ and Carboxylic Acids: a Crystallographic, Spectroscopic and Computational Study

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The direct interaction of MoCl$_5$ with a series of carboxylic acids has been elucidated for the first time. The reactions proceed with release of hydrogen chloride and Cl/O interchange between the metal centre and one equivalent of organic substrate: this feature is unique in the context of the chemistry generally shown by transition metal halides with carboxylic acids. The dinuclear complexes [MoOCl$_2$(κ^1-CX$_3$CO$_2$H)(μ-Cl)]$_2$ (X = H, **1a**; X = Cl, **1b**) and Mo$_2$O$_2$Cl$_6$(μ-CH$_3$CO$_2$H), **2a**, were isolated as the prevalent metal products of the 1:2 molar reactions of MoCl$_5$ with CH$_3$COOH and CCl$_3$COOH. Evidence for the formation of Mo$_2$O$_2$Cl$_6$(μ-CCl$_3$CO$_2$H), **2b**, was achieved by allowing MoCl$_5$ to react with CCl$_3$COOH in 2:3 ratio. Instead the reactions of MoCl$_5$ with a three-fold molar excess of RCOOH afforded the mononuclear complexes MoOCl$_3$(κ^1-RCO$_2$H)$_2$ (R = CH$_3$, **3a**; CCl$_3$, **3b**; CHCl$_2$, **3c**; CMe$_3$, **3d**) in 50-60% yields. The new compounds were characterized by analytical and spectroscopic techniques, moreover the X-ray molecular structures were ascertained for **1a**, **1b** and **2a**; **1a** and **1b** display single Mo–Mo bond. DFT calculations were carried out in order to shed light into structural aspects.

Introduction

The reactions of transition metal chlorides with acetic acid and related halo-α-substituted compounds usually take place *via* the release of hydrogen chloride and may represent an entry into the rich chemistry of carboxylato complexes.[1] This reactivity has been clearly ascertained, *inter alia*, for oxophilic chlorides of metals belonging to the groups 4 [2] and 5.[3] The coordination of the intact carboxylic acid to the metal centre should be considered as the preliminary step of the subsequent activation, however this may not occur in some cases.[3c]

On the other hand, high-valent main group compounds, *i.e.* SOCl$_2$,[4] SiCl$_4$,[2d,5] CCl$_4$,[6] PCl$_3$,[7] POCl$_3$ [8] and PCl$_5$,[9] have been typically employed as effective chlorinating agents towards the carboxylic acid function, to afford acyl chloride derivatives.

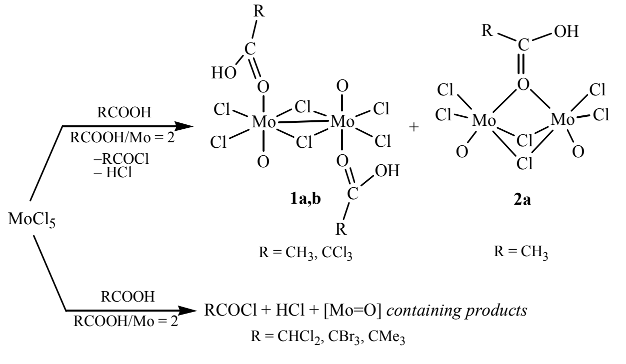
In the framework of our interest in the reactivity of high valent transition metal halides,[10] we have been involved with some unexplored areas of the coordination chemistry of molybdenum pentachloride.[11,12] As a matter of fact, MoCl$_5$ is a versatile, oxophilic, cheap and environmentally acceptable chemical,[13] that has been effectively employed as catalytic precursor for a large variety of organic reactions.[13,14,15] Oxidative transformations of aryls deserve a particular citation: such reactions, which are experiencing a renaissance in synthetic organic chemistry, successfully exploit the unique redox properties of Mo(V) chloride.[14]

Despite this preamble, in general the knowledge of the interaction of MoCl$_5$ with single organic compounds, in the absence of further reactants, has been limitedly elucidated. A possible discouraging drawback may reside in the high moisture sensitivity exhibited by MoCl$_5$, demanding accurately anhydrous reaction systems, and the variety of reaction pathways that may take place when such metal species is allowed to contact with potential ligands.[16,10a,d,e,f] In this context, the only report on the reactivity of MoCl$_5$ with molecules containing the [COOH] functionality referred to the reactions with benzoic acids and stearic acid, which were carried out in variable experimental conditions. The formation of mixed chloro-carboxylate complexes was claimed, in agreement with the general trend observed in the literature (see above). Notwithstanding this hypothesis relied on limited analytical data and unambiguous structural characterization was not supplied.[17] Otherwise carboxylic acids, in combination with MoCl$_5$, may play a crucial role in catalytic reactions: for instance, CCl$_3$COOH was used as effective co-catalyst in the phenylacetylene polymerization by MoCl$_5$, however no explanation was given in terms of possible MoCl$_5$-CCl$_3$COOH interaction.[15e]

In the present paper, we deal with the chemistry of MoCl$_5$ with a selection of carboxylic acids, including acetic acid and halo-α-substituted related compounds. The reactions have been carried out in a weakly coordinating medium (dichloromethane). Analytical, spectroscopic and DFT studies have been carried out in order to elucidate the structures of the metal products. Moreover, NMR experiments have allowed to outline the destiny of the organic substrate.

Results and Discussion

The 1:2 molar reactions of MoCl$_5$ with carboxylic acids afforded mixtures of highly-moisture sensitive metal compounds and the respective acyl chlorides (Scheme 1). According to NMR experiments, nearly one equivalent of RC(O)Cl was produced per mole of Mo. The reactions were accompanied by HCl release, as evidenced by silver chloride precipitation tests (see Experimental).



Scheme 1. The 1:2 reactions of MoCl$_5$ with carboxylic acids.

The production of RC(O)Cl appears to be the result of Cl/O interchange between the metal centre and the organic substrate; coherently, the IR spectra (in the solid state) of the residues obtained by solvent elimination from the reaction mixtures displayed intense absorptions around 1000 cm^{-1}, accounting for the presence of the mono metal-oxido moiety (*vide infra*).[12b-i,18]

The chlorinating behaviour exhibited by molybdenum Mo(V) chloride towards carboxylic acids resembles that of P(V) chloride, rather than reminding the typical chemistry of high-valent transition metal chlorides (see Introduction). In particular, a significant comparison may be traced with $NbCl_5$, that is isostructural with $MoCl_5$: the former selectively reacts with RCOOH (R = CH_3, CCl_3, $CHCl_2$), respectively in 1:1 and 1:2 ratios, to give mixed chloro-carboxylato species, *i.e.* $MoCl_x(O_2CR)_{5-x}$ (x = 3, 4), *via* HCl release.[3]

The unambiguous characterization of metal derivatives from 1:2 $MoCl_5$/RCOOH reactions was possible in a limited number of cases (Scheme 1). Thus the dinuclear complexes $[MoOCl_2(\kappa^1\text{-}CH_3CO_2H)(\mu\text{-}Cl)]_2$, **1a**, and $Mo_2O_2Cl_6(\mu\text{-}CH_3CO_2H)$, **2a**, were identified as the prevalent products of the reaction of $MoCl_5$ with CH_3COOH; analogously, $[MoOCl_2(\kappa^1\text{-}CCl_3CO_2H)(\mu\text{-}Cl)]_2$, **1b**, was obtained from $MoCl_5$/CCl_3COOH in 60% yield. Crystals of **1a**, **1b** and **2a** suitable for X-ray analysis were collected from CH_2Cl_2/hexane mixtures (see Experimental). Actually, compounds **1a** and **2a** co-crystallized as a 1:1 mixture of formula $[MoOCl_2(\kappa^1\text{-}CH_3CO_2H)(\mu\text{-}Cl)]_2\cdot[Mo_2O_2Cl_6(\mu\text{-}\kappa^1\text{-}CH_3CO_2H)]$, **1a·2a**. Since **2a** formally results from the interaction of $MoCl_5$ with 1.5 equivalents of CH_3COOH, we attempted to increase the yield of **2a** by using such stoichiometry; however, the composition of the **1a**/**2a** mixture did not change significantly. The crystals **1a·2a** display intra-molecular hydrogen bonds involving **1a** [O(6)-H(6) 0.86(2) Å; H(6)···Cl(4) 2.82(5) Å; O(6)···Cl(4) 3.439(4) Å; <O(6)H(6)Cl(4) 130(5)°] and **2a** [O(3)-H(3) 0.84 Å; H(3)···Cl(1)#1 2.48 Å; O(3)···Cl(1)#1 3.25(4) Å; <O(3)H(3)Cl(1)#1 152.2°; symmetry transformation #1: -x, y, z], as well as intermolecular H-bonds between **1a** and **2a** [O(6)-H(6) 0.86(2) Å; H(6)···O(1)#6 2.32(6) Å; O(6)···O(1)#6 3.018(6) Å; <O(6)H(6)O(1)#6 138(7)°; symmetry transformation #6: -x+1/2, -y+5/2, -z+1]. The X-ray data of **1a** and **2a** will be separately discussed in the following.

The molecular structure of **1a** is represented in Figure 1 and its relevant bonding parameters are reported in Table 1. **1a** is a dimeric molecule located on 2/m, and only half of molecule is within the asymmetric unit of the unit cell. Its structure is related to those of other $[MoOCl_3L]_2$ (L = thf, Et_2CO, HC(O)OMe, $HC(O)OCH_2CH_2Cl$) dimers previously described in the literature,[11a,d,e,h] except for the unusual occurrence of Mo–Mo bond. In fact, in the previously reported analogous compounds, the Mo–Mo distance falls in the range 3.69-4.06 Å and, thus, is essentially non-bonding. Conversely, the Mo(2)–Mo(2_1) [3.1246(10) Å] distance in **1a** is indicative of a bonding interaction.[11f,i,19,20]

On the other hand, **1a**, likewise $[MoOCl_3L]_2$ (L = thf, Et_2CO, HC(O)OMe, $HC(O)OCH_2CH_2Cl$), contains a perfectly planar $Mo_2(\mu\text{-}Cl)_2$ core with the two Mo(V) centres displaying a distorted octahedral geometry. In the cases of L = thf, Et_2CO, HC(O)OMe, the oxido and one terminal Cl ligand occupy the remaining two equatorial positions on each Mo centre, whereas L and the second Cl ligand are located on the two axial positions. Moreover the terminal equatorial ligands are on the same plane of $Mo_2(\mu\text{-}Cl)_2$ and the μ-Cl bridges are asymmetric in view of their different *trans* ligands. Conversely, in **1a** as well as $[MoOCl_3(HC(O)OCH_2CH_2Cl)]_2$, the oxido and L ligand are in axial positions. The two terminal chlorides occupy the equatorial sites and are considerably out of the $Mo_2(\mu\text{-}Cl)_2$ plane [0.563 Å for **1a**]; the chloride bridges are symmetric, since they are both *trans* to terminal Cl ligands.

Compound **1b** (Figure 2 and Table 2) is very similar to **1a** and will not be discussed any further. Also in this case, the Mo(1)–Mo(1_1) [3.1845(9) Å] distance is indicative of single bond.

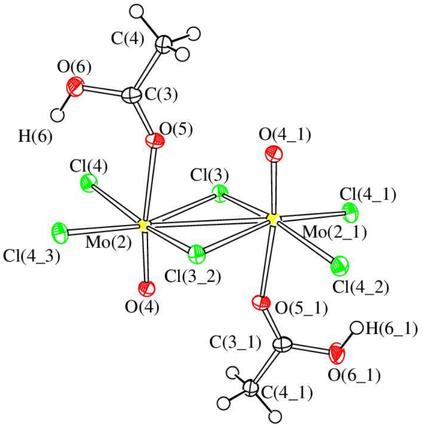


Figure 1. Molecular structure of $[MoOCl_2(\kappa^1\text{-}CH_3CO_2H)(\mu\text{-}Cl)]_2$, **1a**, with key atoms labelled. Thermal ellipsoids are at the 50% probability level. Symmetry operations used to generate equivalent atoms: -x+1, -y+2, -z+1 for Mo(2_1) and the like; x, -y+2, -z+1 for Cl(3_2) and the like; -x+1, y, z for Cl(4_3).

Table 1. Selected bond distances (Å) and angles (°) for **1a**.

Mo(2)–Mo(2_1)	3.1246(10)
Mo(2)–Cl(3)	2.4321(11)
Mo(2)–Cl(4)	2.3475(10)
Mo(2)–O(4)	1.657(4)
Mo(2)–O(5)	2.205(4)
C(3)–C(4)	1.479(8)
C(3)–O(5)	1.217(7)
C(3)–O(6)	1.332(7)
O(4)–Mo(2)–O(5)	171.83(17)
Cl(4)–Mo(2)-Cl(3_2)	164.92(3)
Cl(3)–Mo(2)-Cl(4_3)	164.92(3)
Cl(3)–Mo(2)-Cl(3_2)	100.06(4)
O(5)–C(3)–O(6)	122.3(5)
O(5)–C(3)–C(4)	122.6(5)
C(4)–C(3)–O(6)	115.0(5)

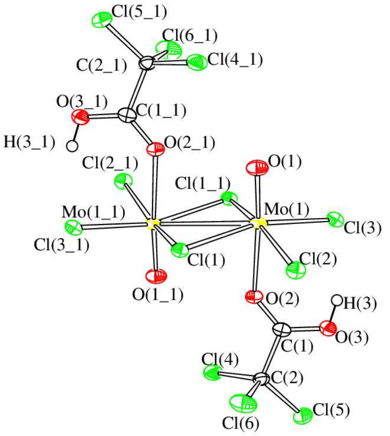


Figure 2. Molecular structure of $[MoOCl_2(\kappa^1\text{-}CCl_3CO_2H)(\mu\text{-}Cl)]_2$, **1b**, with key atoms labeled. Thermal ellipsoids are at the 50% probability level. Symmetry operations used to generate equivalent atoms: -x+1, -y+1, -z+1 for Mo(1_1) and the like.

Table 2. Selected bond distances (Å) and angles (°) for **1b**.

Mo(1)–Mo(1_1)	3.1845(9)
Mo(1)–Cl(1)	2.4173(13)
Mo(1)–Cl(2)	2.3366(12)
Mo(1)–Cl(3)	2.3662(12)

Mo(1)–O(1)	1.643(3)
Mo(1)–O(2)	2.306(3)
C(1)–C(2)	1.540(6)
C(1)–O(2)	1.224(5)
C(1)–O(3)	1.291(5)
O(1)–Mo(1)–O(2)	175.57(14)
Cl(3)–Mo(1)-Cl(1)	164.90(4)
Cl(2)–Mo(1)-Cl(1_1)	162.76(4)
Cl(1)–Mo(1)-Cl(1_1)	97.64(4)
O(2)–C(1)–O(3)	126.7(4)
O(2)–C(1)–C(2)	118.8(4)
C(2)–C(1)–O(3)	114.4(4)

The X-ray structure of **2a** is shown in Figure 3, whereas relevant bond lengths and angles are reported in Table 3. It consists of two face-sharing octahedra with each Mo-centre bonded to one oxido, two terminal and two bridging chloride ligands as well as one bridging CH_3CO_2H. The latter bridging ligand with this coordination mode is rather rare.[21] The Mo(1)–O(1) contact [1.644(4)Å] is considerably shorter than Mo(1)–O(2) [2.442(4) Å], in view of the double bond character of the former and bridging interaction of the latter. The structure of **2a** is related to that of the $[Mo_2O_2Cl_7]^-$ anion previously reported for different salts,[22] being the replacement of a bridging Cl with $\mu\text{-}\kappa^1\text{-}CH_3CO_2H$ the major difference.

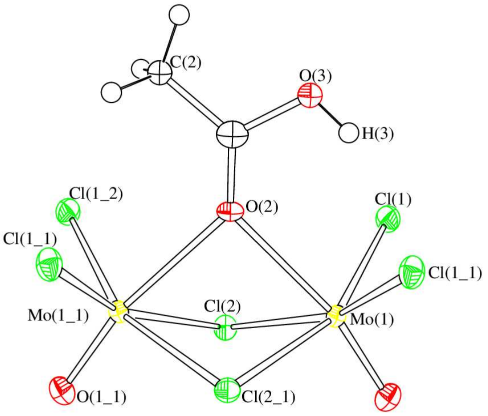


Figure 3. Molecular structure of $Mo_2O_2Cl_6(\mu\text{-}\kappa^1\text{-}CH_3CO_2H)$, **2a**, with key atoms labeled. Thermal ellipsoids are at the 50% probability level. H-bonds are drawn with dashed lines. Symmetry operations used to generate equivalent atoms: -x, y, z for Mo(1_1) and the like; -x, y, -z+3/2 for Cl(1_2).

Table 3. Selected bond distances (Å) and angles (°) for **2a**.

Mo(1)–O(1)	1.644(4)
Mo(1)–O(2)	2.442(4)
Mo(1)–Cl(1)	2.2939(10)
Mo(1)–Cl(2)	2.4776(10)
C(1)–O(2)	1.241(10)
C(1)–O(3)	1.356(8)
C(1)–C(2)	1.488(9)
O(1)–Mo(1)–O(2)	167.69(17)
Cl(1)–Mo(1)-Cl(2_1)	57.62(4)
Cl(2)–Mo(1)–Cl(1_1)	157.62(4)
Cl(2)–Mo(1)–Cl(2_1)	80.00(5)
Mo(1)–O(2)–Mo(1_1)	91.52(18)
O(2)–C(1)–O(3)	119.1(7)
O(2)–C(1)–C(2)	128.1(8)
O(3)–C(1)–C(2)	112.4(9)

The IR spectra (solid state) of **1a-b** and **2a** show diagnostic absorptions due to the OH groups in the range 3100-3330 cm^{-1}, whereas the Mo=O unit manifests itself as a strong band around 1000 cm^{-1}.[12b-i,18] The carbonyl stretching vibration has been found at 1655 and 1694 cm^{-1}, respectively in **1a** and **1b**. The carbonyl absorption is significantly shifted to lower wavenumbers in **2a** (1582 cm^{-1}) compared to **1a**, as consequence of the bridging coordination. Magnetic analysis carried out on **2a** indicated the diamagnetism of this compound, coherently with the X-ray evidence of Mo–Mo single bond (see above).

In order to shed light into structural aspects, we carried out DFT studies. First the structures of **1a**,**b** were calculated, by considering both singlet and triplet states: the calculated structures are shown in the Supporting Information together with relevant bond lengths and angles (Figures S1, S3 and Tables S1, S2). Substantial agreement exists between the singlet state electronic configurations and the corresponding bonding parameters provided by X-Ray (see above), in particular for what concerns the Mo–Mo distances. In other words, DFT calculations strongly support the presence of a single Mo–Mo bond in both **1a** and **1b**, in accordance with the experimental data. Such bond is mainly attributable to the overlapping of d-type orbitals of the metal centres (see Figures S1, S3). Since several isomeric forms are basically predictable for compounds of formula $[MoOCl_2(CX_3CO_2H)(\mu\text{-}Cl)]_2$ (X = H, Cl), we calculated structures differing from **1a,b** in the relative orientation of the oxygen ligands (Figures S2, S4). The geometries corresponding to **1a** and **1b**, *i.e.* those detected by X-ray, resulted the most stable ones in the respective cases (see Graphs within Figures S2, S4).

Also the structure of **2a** was optimized by DFT calculations. The calculated structure of **2a** in triplet state (Figure S5 and Table S3) resulted coherent with the one determined by X-ray diffractometry.[23]

In order to evaluate the possibility that a compound analogous to **2a** could be obtained from $MoCl_5/CCl_3COOH$, we optimized the structure of the hypothetical complex $Mo_2O_2Cl_6(\mu\text{-}CCl_3CO_2H)$, **2b**. All the geometry optimizations carried out from starting structures comparable to that of **2a** led to a drastic change of the coordination mode of the CCl_3COOH ligand, due to both electronic and steric factors. In fact the donor ability of the C=O moiety belonging to CCl_3COOH is lower than that related to CH_3COOH, as suggested by the Mulliken charges on the sp^2 oxygen atoms in the non coordinated molecules (–0.450 and –0.394 a.u. according to EDF2 calculations; –0.512 and –0.441 a.u. according to M06 functional, respectively for CH_3COOH and CCl_3COOH). Moreover, even steric interactions between the $[CCl_3]$ fragment and the Cl-ligands contribute to disfavour for **2b** the arrangement found in **2a**. The CCl_3COOH coordination to one single metal centre appeared possible, on considering both singlet and triplet state electronic configurations (Figure S6, structure **2bA**). Nevertheless, the most stable structure calculated for **2b** resulted to comprise a CCl_3COOH ligand $\mu\text{-}\kappa^2$-coordinated to a dinuclear frame not exhibiting Mo–Mo bond (Figures 4-S6, Table S4).[24]

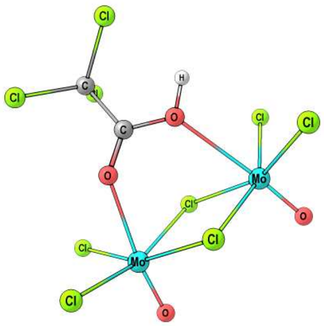


Figure 4. Lowest energy structure calculated for **2b**.

Evidence for the formation of **2b** was collected by allowing $MoCl_5$ to react with CCl_3COOH in the appropriate stoichiometry (2:3 molar ratio). In these conditions, a mixture of **1b** and a second metal compound was isolated after work-up. The IR band (solid state spectrum) occurring at 1751 cm^{-1} agreed with the presence of **2b**, since significant increase of the carbonyl stretching vibration wave number has been predicted on going from **1b** to **2b**.

Compounds of the type **1** consist of dinuclear structures bearing Cl-bridges which are expected to be broken by the addition of further amounts of oxygen donor.[11g,h] In this light, we tried the reaction of **1a** with acetic acid in dichloromethane. The reaction led to the good-yield isolation of a complex of formula $MoOCl_3(CH_3CO_2H)_2$, **3a** (according to elemental analysis). **3a** was directly obtained by the treatment of $MoCl_5$ with a three-fold excess of acetic acid in dichloromethane (Scheme 2). By similar procedures, the products $MoOCl_3(L)_2$ (L = CCl_3CO_2H, **3b**; $CHCl_2CO_2H$, **3c**; CMe_3CO_2H, **3d**) were isolated in 52-57% yields (Scheme 2). Instead the 1:3 reaction of $MoCl_5$ with CBr_3COOH led to a mixture of products whose identity could not be defined. The formation of **3a-d** was accompanied by production of the relevant acyl-chloride and release of HCl (see Experimental).

$$MoCl_5 \xrightarrow[\substack{RCOOH/Mo = 3\\ -RCOCl\\ -HCl}]{RCOOH} MoOCl_3(RCOOH)_2$$

$$R = CH_3,\ \mathbf{3a};\ CCl_3,\ \mathbf{3b},\ CHCl_2,\ \mathbf{3c},\ CMe_3,\ \mathbf{3d}$$

Scheme 2. Synthesis of molybdenum(V) oxido-complexes from the 1:3 molar reactions of $MoCl_5$ with carboxylic acids.

The IR spectra of **3a** and **3b** (in the solid state) displayed two absorptions attributed to the carbonyl groups (*e.g.* at 1675 and 1620 cm^{-1}, in the case of **3a**), in agreement with the respective simulated spectra. The band due to the Mo=O moiety was seen at *ca.* 990 cm^{-1}. The IR spectra of **3c,d** exhibited analogous features. Magnetic analyses carried out on **3a-d** provided μ_{eff} values (calculated per Mo atom) around 1.60 BM, in strict accordance with what previously reported for similar mononuclear Mo(V) oxido-chloride complexes.[12b-h]

Possible structures were considered and thus calculated for **3a** and **3b**; they are shown in the SI (Figures S7-S8 and Tables S5-S6). In both cases, the most stable form comprises a mutual *cis* arrangement of the two organic ligands and the oxido moiety *trans*-located to one of them (Figure 5); this configuration is that presumably adopted by complexes of type **3**.

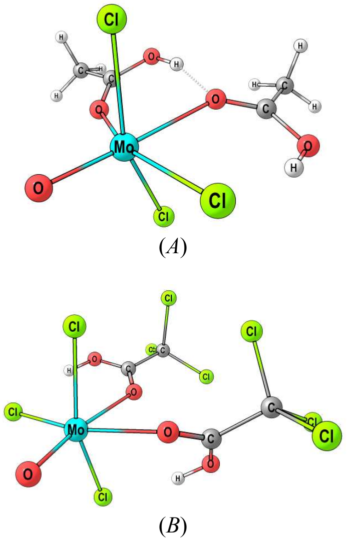


Figure 5. Lowest energy structures calculated for $MoOCl_3(\kappa^1-CH_3COOH)_2$, **3a** (A), and $MoOCl_3(\kappa^1-CCl_3COOH)_2$, **3b** (B), respectively.

Conclusions

Although a large amount of information have appeared in the literature on the reactivity of halides of high-valent elements with carboxylic acids, this piece of chemistry was almost unexplored for what concerns molybdenum pentachloride. Our results demonstrate that the behaviour of $MoCl_5$, when allowed to contact with (halo)acetic acids, well parallels the chlorinating power of high-valent main group chlorides, rather than what observed with high-valent transition metal chlorides in general. This point is presumably related to the relatively weak Mo–Cl bond,[25,26] thus allowing the occurrence of the Cl/O interchange process in mild conditions.

The reactions lead to mixtures of highly-moisture sensitive Mo(V) complexes, whose structural characterization has been possible on the basis of combined experimental and DFT data. The outcomes of this research contribute to expand the knowledge on the coordination chemistry of $MoCl_5$, and hopefully to the development of the $MoCl_5$-relevant inorganic and organic synthesis.

Experimental

General

Warning: all the metal products reported in this paper are highly moisture-sensitive, thus rigorously anhydrous conditions were required for the reaction and crystallization procedures. The reaction vessels were oven dried at 140°C prior to use, evacuated (10^{-2} mmHg) and then filled with argon. $MoCl_5$ was purchased from Strem (99.6% purity) and stored in sealed tubes under argon atmosphere. Once isolated, the metal products were conserved in sealed glass tubes under argon. The organic reactants were commercial products (Sigma-Aldrich) stored under argon atmosphere as received. Solvents (Sigma-Aldrich) were distilled before use from appropriate drying agents. Infrared spectra were recorded at 298 K on a FT IR-Perkin Elmer Spectrometer, equipped with a UATR sampling accessory. Magnetic susceptibilities (reported per Mo atom) were measured at 298 K on solid samples with a Magway MSB Mk1 magnetic susceptibility balance (Sherwood Scientific Ltd.). Diamagnetic corrections were introduced according to König.[27] NMR spectra were recorded at 293 K on a Bruker Avance DRX400 instrument equipped with a BBFO broadband probe. The chemical shifts were referenced to the non-deuterated aliquot of the solvent. Carbon and hydrogen analyses were performed on a Carlo Erba mod. 1106 instrument. The halide content was determined by the Mohr method [28] on solutions prepared by dissolution of the solids in aqueous KOH and heated at boiling temperature for 72 hours, followed by cooling to room temperature and addition of HNO_3 up to neutralization.

Reactions of $MoCl_5$ with carboxylic acids: identification of acyl chlorides and HCl.

General procedure: $MoCl_5$ (0.137 g, 0.500 mmol), CD_2Cl_2 (0.60 mL) and the appropriate organic reactant (0.500 mmol) were introduced into a NMR tube in the order given. The tube was sealed, briefly shaken in order to homogenize the content, and maintained at room temperature for 5 d. Hence the resulting solution was analyzed by NMR. When the tube was opened, gas (HCl) release was observed: bubbling the gas into an aqueous solution of $AgNO_3$ determined precipitation of a white solid (AgCl).

a) From $MoCl_5/CH_3CO_2H$. ^1H NMR (CD_2Cl_2): δ = 2.70 (s, CH_3COCl) ppm.[29]

b) From $MoCl_5/CCl_3CO_2H$. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 163.9 (CCl_3COCl), 94.5 (CCl_3COCl) ppm.[30]

c) From $MoCl_5/CBr_3CO_2H$. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 164.7 (CBr_3COCl), 36.8 (CBr_3COCl) ppm.

d) From $MoCl_5/CHCl_2CO_2H$. ^1H NMR (CD_2Cl_2): δ = 6.23 (s, $CHCl_2COCl$) ppm.[29] $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 167.4 ($CHCl_2COCl$), 71.4 ($CHCl_2COCl$) ppm.

e) From $MoCl_5/Me_3CCO_2H$. ^1H NMR (CD_2Cl_2): δ = 1.33 (s, CMe_3COCl) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 187.1 (CMe_3COCl), 39.1 (CMe_3COCl), 26.9 (CMe_3COCl) ppm.

The same results were substantially obtained from the analogous reactions of $MoCl_5$ (*ca.* 0.50 mmol) with, respectively, two and three equivalents of carboxylic acids.

Synthesis and isolation of molybdenum complexes. *General procedure*: a suspension of $MoCl_5$ in CH_2Cl_2 (*ca.* 20 mL) was treated with the appropriate organic reactant. The mixture was allowed to stir at room temperature for 24 h. The final solution was concentrated to *ca.* 5 mL, layered with hexane and settled down at −30 °C. A solid was collected after one-two weeks.

1) Reactions of $MoCl_5$ with CH_3CO_2H: synthesis of $[MoOCl_3(\kappa^1\text{-}CH_3CO_2H)]_2$, 1a, $Mo_2O_2Cl_6(\mu\text{-}\kappa^1\text{-}CH_3CO_2H)$, 2a, and $MoOCl_3(\kappa^1\text{-}CH_3CO_2H)_2$, 3a. Compounds **1a** and **2a** were afforded as a mixture of dark-green crystals, from $MoCl_5$ (0.320 g, 1.17 mmol) and CH_3CO_2H (0.135 mL, 2.36 mmol). Anal. Calcd for $C_6H_{12}Cl_{12}Mo_4O_{10}$,(**1a·2a**): C, 6.84; H, 1.15; Cl, 40.39. Found: C, 6.74; H, 1.03; Cl, 40.11. Yield 0.178 g. IR (solid state): ν = 3329br (ν_{O-H}), 3140br (ν_{O-H}), 1655vs ($\nu_{C=O}$, **1a**), 1582vs ($\nu_{C=O}$, **2a**), 1395m, 1357m, 1325w-m, 1231s, 1205w-m, 1046w, 1005vs ($\nu_{Mo=O}$, **1a**), 993vs ($\nu_{Mo=O}$, **2a**), 904m, 726w, 669m cm^{-1}.

The reaction of $MoCl_5$ (0.270 g, 0.988 mmol) with CH_3CO_2H (0.283 mL, 4.95 mmol) led to the isolation of a dark-green solid corresponding to **3a**. Yield 0.197 g, 59%. Anal. Calcd for $C_4H_8Cl_3MoO_5$: C, 14.20; H, 2.38; Cl, 31.43. Found: C, 14.30; H, 2.34; Cl, 31.29. IR (solid state): ν = 3156m-br, 2354w, 1675s ($\nu_{C=O}$), 1620s ($\nu_{C=O}$), 1522m, 1441vs, 1400vs, 1350s, 1256w, 1221m, 1210m, 1083w, 1046w, 985vs ($\nu_{Mo=O}$), 948s-sh, 915w, 809m, 729vs, 699vs, 683vs cm^{-1}. Magnetic measurement: χ_M^{corr} = 9.94×10^{-4} cgsu, μ_{eff} = 1.55 BM.

2) Reactions of $MoCl_5$ with CCl_3CO_2H: synthesis of $[MoOCl_3(\kappa^1\text{-}CCl_3CO_2H)]_2$, 1b, and $MoOCl_3(\kappa^1\text{-}CCl_3CO_2H)_2$, 3b, and possible isolation of $Mo_2O_2Cl_6(\mu\text{-}CCl_3CO_2H)$, 2b. Compound **1b** was isolated as dark-brown solid from $MoCl_5$ (0.305 g, 1.12 mmol) and CCl_3CO_2H (0.227 mL, 2.25 mmol). Yield 0.256 g, 60%. Anal. Calcd for $C_2HCl_6MoO_3$: C, 6.29; H, 0.26; Cl, 55.73. Found: C, 6.36; H, 0.40; Cl, 55.49. IR (solid state): ν = 3138br (ν_{O-H}), 1694vs ($\nu_{C=O}$), 1426w, 1392w-m, 1192w-m, 1011vs ($\nu_{Mo=O}$), 956m, 853vs, 819s, 710m-s, 678vs cm^{-1}. Magnetic measurement: diamagnetic.

The reaction of $MoCl_5$ (0.480 g, 1.76 mmol) with CCl_3CO_2H (0.266 mL, 2.64 mmol) yielded, after work-up, **1b** in admixture with a minor product identified as **2b**. Yield 0.508 g. IR (solid state): ν = 1751 ($\nu_{C=O}$, **2b**), 995 ($\nu_{Mo=O}$, **2b**) cm^{-1}.

3b was obtained as a brown solid from $MoCl_5$ (0.305 g, 1.12 mmol) and CCl_3CO_2H (0.555 mL, 5.50 mmol). Yield 0.348 g, 57%. Anal. Calcd for $C_4H_2Cl_9MoO_5$: C, 8.81; H, 0.37; Cl, 58.54. Found: C, 8.95; H, 0.46; Cl, 58.29. IR (solid state): ν = 2963w, 2904w, 1639m ($\nu_{C=O}$), 1610s ($\nu_{C=O}$), 1385vs, 1367vs, 1260w-m, 1088w-m, 1042w, 988vs ($\nu_{Mo=O}$), 848vs, 829vs, 737s, 683vs cm^{-1}. Magnetic measurement: χ_M^{corr} = 1.04×10^{-3} cgsu, μ_{eff} = 1.58 BM.

3) Reaction of $MoCl_5$ with $CHCl_2CO_2H$: synthesis of $MoOCl_3(\kappa^1\text{-}CHCl_2CO_2H)_2$, 3c. Compound **3c** was obtained as light-green solid from $MoCl_5$ (0.350 g, 1.28 mmol) and $CHCl_2CO_2H$ (0.634 mL, 7.69 mmol). Yield 0.317 g, 52%. Anal. Calcd for $C_4H_4Cl_7MoO_5$: C, 10.09; H, 0.85; Cl, 52.12. Found: C, 10.14; H, 1.01; Cl, 51.97. IR (solid state): ν = 3012w, 2982w, 1615vs ($\nu_{C=O}$), 1567s ($\nu_{C=O}$), 1415s, 1398vs, 1223m-s, 1207w, 995vs ($\nu_{Mo=O}$), 985m-sh, 967s, 819s, 789m.s, 757s, 716s, 700s, 657m cm^{-1}. Magnetic measurement: χ_M^{corr} = 1.12×10^{-3} cgsu, μ_{eff} = 1.64 BM.

4) Reaction of $MoCl_5$ with CMe_3CO_2H: synthesis of $MoOCl_3(\kappa^1\text{-}CMe_3CO_2H)_2$, 3d. Compound **3d** was obtained as brown solid from $MoCl_5$ (0.290 g, 1.06 mmol) and CMe_3CO_2H (0.511 mL, 4.45 mmol). Yield 0.255 g, 57%. Anal. Calcd for $C_{10}H_{20}Cl_3MoO_5$: C, 28.42; H, 4.77; Cl, 25.17. Found: C, 28.29; H, 4.65; Cl, 25.31. IR (solid state): ν = 2972w, 2931w, 2870w, 1651m ($\nu_{C=O}$), 1610m ($\nu_{C=O}$), 1573w, 1537m-s, 1480s, 1424m, 1404w, 1359m, 1260w-m, 1220m, 1193m, 1153m, 1079s, 1017s, 989vs ($\nu_{Mo=O}$), 974s, 904m, 796vs, 781s, 745vs cm^{-1}. Magnetic measurement: χ_M^{corr} = 1.15×10^{-3} cgsu, μ_{eff} = 1.67 BM.

X-ray crystallographic studies. Crystal data and collection details for $[MoOCl_2(\kappa^1\text{-}CH_3CO_2H)(\mu\text{-}Cl)]_2\cdot[Mo_2O_2Cl_6(\mu\text{-}\kappa^1\text{-}CH_3CO_2H)]$, **1a·2a**, and $[MoOCl_2(\kappa^1\text{-}CCl_3CO_2H)(\mu\text{-}Cl)]_2$, **1b**, are reported in Table 1. The diffraction experiments were carried out on a Bruker APEX II diffractometer equipped with a CCD detector and using Mo-Kα radiation (λ = 0.71073 Å). Data were corrected for Lorentz polarization and absorption effects (empirical absorption correction SADABS).[31] Structures were solved by direct methods and refined by full-matrix least-squares based on all data using F^2.[32] All non-hydrogen atoms were refined with anisotropic displacement parameters. H-atoms were placed in calculated positions and treated isotropically using the 1.2 fold U_{iso} value of the parent atom except methyl protons, which were assigned the 1.5 fold U_{iso} value of the parent C-atom. The O-bonded hydrogen atoms were initially located in the Fourier map but, then, they were refined with a riding model, apart from H(6) in **1a** which was refined isotropically, using the 1.5 fold U_{iso} value of the parent O(6).

A 1:1 mixture of **1a** and **2a** is present within the unit cell of $[MoOCl_2(\kappa^1\text{-}CH_3CO_2H)(\mu\text{-}Cl)]_2\cdot[Mo_2O_2Cl_6(\mu\text{-}\kappa^1\text{-}CH_3CO_2H)]$, **1a·2a**. In addition, considering the asymmetric unit out the unit cell, this contains half of a molecule of **1a** (located on 2/m) and half of a molecule of **2a** (located on m2m). The O(3)H(3) and C(2)H_3 groups of **2a** are disordered over four equally populated symmetry related (by m2m) positions and, thus, the independent part was refined with 0.25 occupancy factor. Similar *U* restraints (s.u. 0.01) were applied to the C and O atoms of **1a·2a**. Restraints to bond distances were applied as follows (s.u. 0.02): 1.51 Å for C(1)–C(2) and 1.35 Å for C(1)–O(3) in **2a**; 0.87 Å for O(6)–H(6) in **1a**. The asymmetric unit of the unit cell of **1b** contains half of a molecule located on an inversion centre.

Insert Table 4 about here

Computational studies. Preliminary computational geometry optimization of the complexes was carried out without symmetry constrains, using the hybrid DFT EDF2 functional [33] in combination with the LACVP** basis set. The latter is a combination of the 6-31G(d,p) basis set with the LANL2DZ effective core basis set.[34] Further geometry optimization was performed using the hyper-GGA functional M06 [35] in combination with the 6-31G(d,p) basis sets on H, C, O and Cl atoms and the ECP-based polarized LANL2TZ(f) basis set on Mo.[36] C-PCM implicit solvation model for dichloromethane was added to M06 calculations.[37] In all of the cases the stationary points were characterized by IR simulations, from which zero-point vibrational energies and thermal corrections were obtained. The "unrestricted" formalism was applied for calculations on paramagnetic systems.[38] DFT-simulated IR data, obtained with harmonic approximation, assisted the interpretation of experimental IR spectra. The software used for EDF2 calculations was Spartan 08,[39] while M06/C-PCM optimizations were carried out with Gaussian 09.[40]

Supporting Information. Figures S1-S8 show the DFT-calculated structures discussed in this paper. Tables S1-S6 contain the relevant computed bonding parameters. CCDC reference numbers 1015025 (**1a•1b**) and 1015026 (**2a**) contain the supplementary crystallographic data for the X-ray studies reported in this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; e-mail: deposit@ccdc.cam.ac.uk].

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Table 4. Crystal data and details of the structure refinement for [MoOCl$_2$(κ^1-CH$_3$CO$_2$H)(μ-Cl)]$_2$·[Mo$_2$O$_2$Cl$_6$(μ-κ^1-CH$_3$CO$_2$H)], **1a·2a**, and [MoOCl$_2$(κ^1-CCl$_3$CO$_2$H)(μ-Cl)]$_2$, **1b**.

Complex	**1a·2a**	**1b**
Formula	$C_6H_{12}Cl_{12}Mo_4O_{10}$	$C_4H_2Cl_{12}Mo_2O_6$
Fw	1053.32	763.34
T, K	100(2)	100(2)
λ, Å	0.71073	0.71073
Crystal system	Orthorhombic	Triclinic
Space group	*Cmcm*	$P\bar{1}$
a, Å	9.8719(15)	5.9376(17)
b, Å	7.9597(12)	7.406(2)
c, Å	34.729(5)	12.038(4)
α, °	90	83.082(3)
β, °	90	88.495(3)
γ, °	90	75.691(3)
Cell Volume, Å^3	2728.9(7)	509.2(3)
Z	4	1
D_c, g cm^{-3}	2.564	2.489
μ, mm^{-1}	3.010	2.824
F(000)	2000	362
Crystal size, mm	0.24×0.18×0.14	0.22×0.19×0.12
θ limits, °	2.35–25.03	1.70–27.00
Reflections collected	12125	5458
Independent reflections	1281 [R_{int} = 0.0400]	2208 [R_{int} = 0.0413]
Data / restraints /parameters	1281 / 39 / 96	2208 / 0 / 109
Goodness on fit on F^2	1.337	1.060
R_1 ($I > 2\sigma(I)$)	0.0275	0.0434
wR_2 (all data)	0.0635	0.1183
Largest diff. peak and hole, e Å^{-3}	0.625 / –0.747	2.306 / –1.474