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PAPER

Mononuclear anionic AO₂X₃ compounds with non-VSEPR structure†

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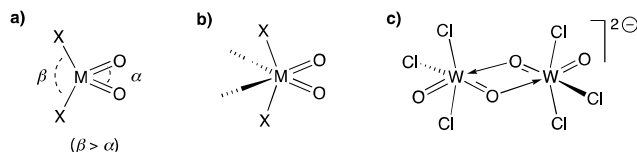
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5 The molybdenyl compound [NBu₄][MoO₂(C₆F₅)₃] (**1**) has been obtained by low-temperature treatment of MoO₂Cl₂ with LiC₆F₅ in Et₂O followed by addition of [NBu₄]Br. This compound of the (AO₂X₃)[□] type shows an unusual five-coordinate structure not lying on the Berry-pseudorotation path: it can be described rather as an edge-caped tetrahedron (*TE*-5). The same kind of structure has been found by DFT calculations to be the most energetically favored for the mononuclear (MoO₂X₃)[□] model species, where
10 X = H, Cl or CN. Compound **1** exhibits marked stereochemical stability, as it shows no sign of exchange between chemically inequivalent C₆F₅ groups even at 150 °C in dmf solution (¹⁹F NMR spectroscopy).

Introduction

Neutral, closed-shell MO₂X₂ oxohalides are typical of Group 6 metals¹ with the central atom bearing the group valence.² These
15 compounds are good oxidants with wide use in chemical synthesis³ and are also involved in chemical transport processes of great technical importance.⁴ Among the possible M/X combinations, only the chloro-series is sufficiently stable for all three Group 6 metals.^{5–8} They all have approximate tetrahedral
20 (*T*-4) structure as isolated molecules (Scheme 1a).⁹ Essentially the same *T*-4 structure is preserved for CrO₂Cl₂ in the solid state,¹⁰ whereas for the heavier homologues MoO₂Cl₂⁶ and WO₂Cl₂,¹¹ extended lattices are found, in which the metal centres achieve six-coordinate environments as the result of extended
25 bridging systems (Scheme 1b).^{§12,13} The different degrees of intermolecular association observed in the solid state, denote different Lewis acidity for the corresponding d⁰ metal centres. Accordingly, CrO₂Cl₂ shows no affinity for any additional Cl[□] ligand,¹⁴ while the heavier metals form [MO₂Cl₃][□] compounds.¹⁵
30 Even these anionic units are further associated, as in dimeric [PPh₄]₂[(WO₂Cl₃)₂]¹⁶ (Scheme 1c),^{¶17,18} or bind an additional ligand, as in [MoO₂Cl₃(OH₂)][□],^{#19,20} rendering again the metal six-coordinate. Only for the Group 16 related species (SO₂F₃)[□] has a monomeric structure been assigned on the basis of
35 vibrational data.²¹



Scheme 1. Structures of discrete MO₂X₂ molecules for Group 6 metals (a) and in condensed phase for the heavier ones (b), as well as that of the anion of [PPh₄]₂[(WO₂Cl₃)₂] (c).¹⁶

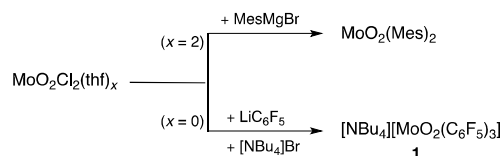
40 The organomolybdenum [MoO₂(C₆F₅)₃][□] derivative presented here is, as far as we know, the first mononuclear (AO₂X₃)[□]

compound to have been structurally characterized for any chemical element.

Results and Discussion

Synthesis and characterization

The molybdenyl chloride adduct MoO₂Cl₂·2thf is known to react (Scheme 2) with mesityl Grignard, MesMgBr, affording the neutral organomolybdenum(vi) compound MoO₂(Mes)₂,^{22a} which exhibits an approximate *T*-4 geometry (Scheme 1a).^{22b} We have
50 now found that the unsolvated oxychloride MoO₂Cl₂ reacts with the organolithium derivative LiC₆F₅ giving rise, under subsequent addition of [NBu₄]Br, to an anionic organomolybdenum(vi) species that is isolated as the salt [NBu₄][MoO₂(C₆F₅)₃] (**1**) in reasonable yield (Scheme 2). Our attempts to prepare the
55 analogous tungsten derivative starting from WO₂Cl₂ and working under similar conditions failed, probably due to the insolubility and the comparatively lesser reactivity of the starting material. Eventually no pentafluorophenyl-tungsten compound was detected among the reaction products.



Scheme 2. Synthetic procedures affording aryl-derivatives of molybdenyl (Mes = mesityl).

Compound **1** is a thermally robust solid only decomposing at *ca.* 210 °C. It has been characterized by analytical and
65 spectroscopic methods and its crystal and molecular structures have been established by single-crystal X-ray diffraction techniques. The crystal lattice of 1·¼CH₂Cl₂ is made of separate ions with no significant cation/anion interaction and with additional solvent molecules interspersed. The molybdenum
70 center in the mononuclear anion [MoO₂(C₆F₅)₃][□] (Fig. 1) is surrounded by two terminal oxo ligands and three σ-bonded C₆F₅

groups with no sign of any intramolecular F \cdots Mo interaction. The three Mo–C bonds have indistinguishable lengths (220.7(5) pm, average) regardless of their respectively different locations in the molecule. The plane defined by the MoC₃ fragment is virtually perpendicular to the MoO₂ unit (dihedral angle: 88.8°), almost bisecting it: O(1)–Mo–C(7) 124.8(2)° vs. O(2)–Mo–C(7) 121.5(2)°. The structure of this five-coordinate unit could be routinely described as a “distorted trigonal bipyramid”. The distortion, however, does not lie on the Berry-pseudorotation path connecting the two polytopes most usually found in five-substituted compounds of both metals and non-metals (Scheme 3).²³ The pseudo-axial C₆F₅ groups deviate from linearity (C(1)–Mo–C(13) 152.2(2)°) not toward the pseudo-equatorial oxo ligands but rather away from them. Considering this important structural feature together with the fact that the O–Mo–O angle (113.6(2)°) does not significantly depart from an ideal tetrahedral angle (109.5°), we consider the structure to be best described as an edge-capped tetrahedron (*TE-5*).²⁴ In fact, continuous shape measures (CShM)²⁵ show that the normalized shape of the [MoO₂(C₆F₅)₃][–] anion lies almost halfway between a tetrahedron (*T-4*) and a trigonal bipyramid (*TBPY-5*) with just 1% deviation from the ideal path connecting both geometries (Fig. 2).²⁶

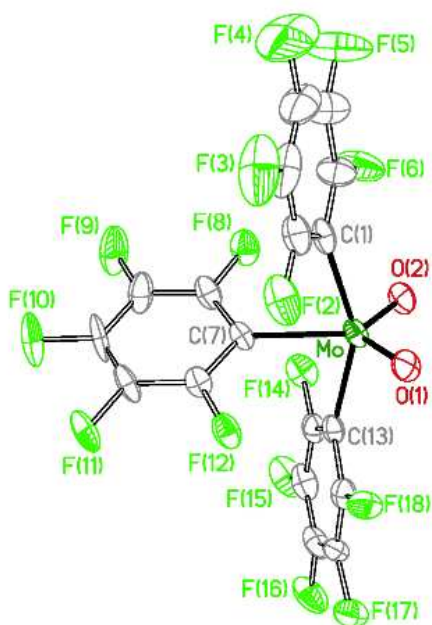
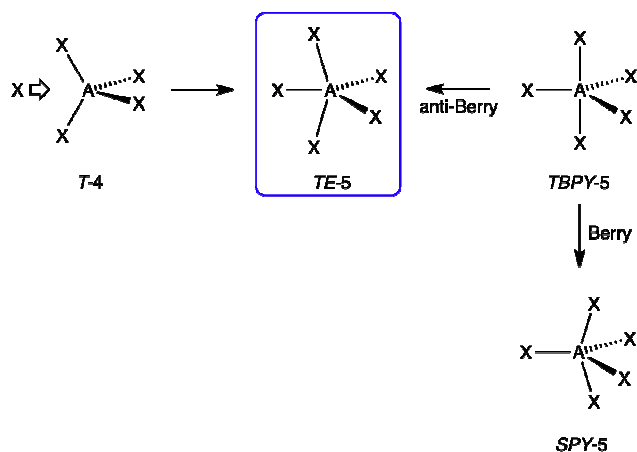


Fig. 1 Displacement-ellipsoid diagram (50% probability) of the [MoO₂(C₆F₅)₃][–] anion as found in single crystals of 1·½CH₂Cl₂. Selected bond lengths [pm] and angles [°] with estimated standard deviations: Mo–O(1) 168.9(3), Mo–O(2) 169.4(3), Mo–C(1) 219.9(5), Mo–C(7) 222.1(4), Mo–C(13) 220.2(4), O(1)–Mo–O(2) 113.6(2), O(1)–Mo–C(7) 124.8(2), O(2)–Mo–C(7) 121.5(2), C(1)–Mo–C(7) 76.4(2), C(1)–Mo–C(13) 152.2(2), C(7)–Mo–C(13) 76.0(2).

The *TE-5* geometry was first identified by Ward and coworkers,²⁷ who suggested it to be associated with the presence of two strong π -donors on the non-capped edge, as is the case of the oxo ligand. Significantly wider O–M–O angles were found in the related neutral organorhenium(VII) compounds ReO₂(CH₂tBu)₃ (117.4(5)°)^{28a} and ReO₂Me₃ (123.0(20)°).^{28b} It is, however, difficult to evaluate to what extent the intramolecular α -C–H \cdots O interactions found in the crystal structure of the former

species^{28a} and the C–H \cdots Re agostic interactions identified in the gas-phase structure of the latter (obtained by electron diffraction)^{28b} might alter the corresponding structural features. It is interesting to note that no similar intramolecular interaction or additional intermolecular association of any kind have been found in the [MoO₂(C₆F₅)₃][–] anion.



Scheme 3 Two opposed distortion paths on a *TBPY-5* structure, together with the formal relationship of the less-common *TE-5* polytope with the *T-4* geometry. No indication of charges is intended.

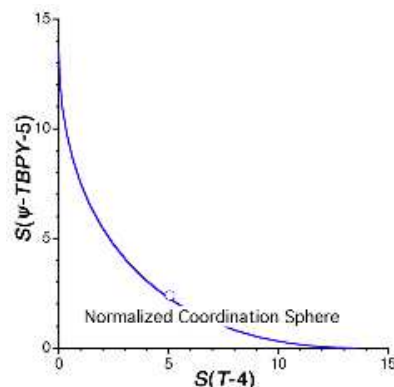


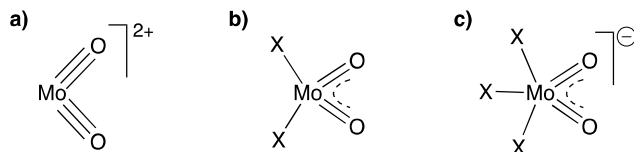
Fig. 2 Shape map showing the position of the five-coordinate [MoO₂(C₆F₅)₃][–] anion as found in compound **1** with respect to the minimum distortion path (blue line) connecting the *T-4* and ψ -*TBPY-5* polyhedra through ligand association/dissociation (Scheme 3, left).²⁶

Theoretical calculations on model and real systems

In principle, compound **1** can be considered to derive from the neutral derivative MoO₂(C₆F₅)₂ by association of an additional C₆F₅ group (Scheme 3, left). Our attempts to prepare this neutral compound by 1:2 reaction of MoO₂Cl₂ with the Grignard reagent C₆F₅MgBr in Et₂O failed, giving instead magnesium salts of the [MoO₂(C₆F₅)₃][–] anion, as identified by IR, ¹⁹F NMR and X-ray fluorescence spectroscopy. The structure of the putative, non-isolated precursor species MoO₂(C₆F₅)₂ (**DFT-b**) has been optimized by DFT methods (see ESI for details).[†] The approximately *T-4* geometry obtained (Fig. S1)[†] is similar to that experimentally observed for gaseous MoO₂Cl₂²⁹ and for solid MoO₂(Mes)₂.^{22b} None of these structures conform with the VSEPR model, since in all of them $\beta > \alpha$ (Table S1).^{†30}

It is worth noting that the structural parameters of the (MoO₂)²⁺ unit show little variation within the wealth of known

molybdenyl compounds, regardless of the different coordination environments.³¹ In our opinion, this apparent insensitivity denotes the special stability associated with the *cis*-(MoO₂)²⁺ unit and justifies its traditional formulation as a defined chemical entity: molybdenyl. *Ab initio* calculations suggest that the singlet, bent (MoO₂)²⁺ unit (Scheme 4a) may even have “an autonomous existence”.³²



Scheme 4 Schematic drawing of the naked molybdenyl unit (a),³² the neutral, isolated MoO₂X₂ molecules (b) and the mononuclear [MoO₂X₃][−] anion (c) with indication of the Mo–O bond order in each case.

An analysis of the bonding orbitals in the MoO₂(C₆F₅)₂ molecule enables to identify 2σ + 3π bonding orbitals as mainly involved in the MoO₂ bonding system (Fig. S2),[†] resulting in a formal bond order of 2.5 for each Mo–O bond (Scheme 4b).³³ We have also found that by forcing a gradual widening of the β angle in the lower-energy geometry of MoO₂(C₆F₅)₂ a well-defined LUMO emerges with the appropriate symmetry to allow the coordination of an additional ligand near the midpoint of the C–C edge (Fig. 3). Similar results have been obtained by widening the β angle in other MoO₂X₂ molecules with X = H, Cl or CN, as typical representatives of ligands with sharply different donor abilities. In all these cases, the coordination of an additional X ligand also results in the corresponding (MoO₂X₃)[−] anionic species, for which similar *TE*-5 geometries have been found to be the most energetically favored (Fig. S5).[†] This common behavior suggests that five-coordinate species with a *TE*-5 structure—that has generally been overlooked—might play an important role in the chemistry of molybdenyl. Indeed, the structure of the mixed-ligand [MoO₂(Mes)Me₂][−] anion, originally described as a distorted *TBPY*-5,³⁴ displays features related to those found in compound **1**, despite the oxo ligands in the former strongly interact with the [Li(OEt)₂]⁺ cations building Mo–O–Li bridges. This strong cation/anion interaction might well be the reason for the wide O–Mo–O angle observed (119.53(8)°), which largely departs from the tetrahedral value.

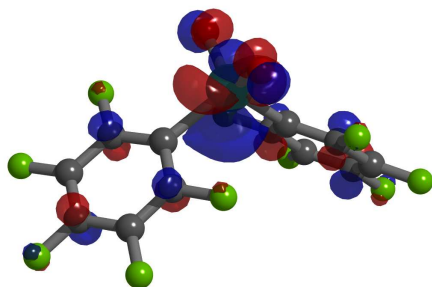


Fig. 3 Lowest unoccupied molecular orbital (LUMO) in compound **1** (cf. Fig. S4).[†]

The VSEPR model, which is a simple and invaluable tool to predict and rationalize the stereochemistry of a wealth of main-group derivatives,³⁵ has proven of little use for transition metal compounds having non-spherical cores (*i.e.*, those in which the

central atom has a partially occupied d shell). Nevertheless, the model should still apply for molecules in which the metal atom has a spherical core. The anion of **1** adds now to the notable exceptions documented for empty-shell d⁰ compounds.³⁰ The VSEPR model assumes that multiple bonds exert higher repulsion towards neighbor electron pairs than single bonds and hence the O–A–O angle in a mononuclear AO₂X₃ species should be wider than 120°. In line with this reasoning, a value of 129.1° has been calculated for the O–S–O angle in the (SO₂F₃)[−] anion.^{21a} In contrast, however, a significantly narrower angle (113.6(2)°) has been experimentally found for the O–Mo–O unit in the anion of **1**. In view of this disparity, a theoretical treatment of the latter species seemed appropriate.

The geometry of the [MoO₂(C₆F₅)₃][−] anion, as optimized by DFT methods (Fig. S5),[†] shows excellent agreement with the experimental one including the narrow O–Mo–O angle (Table S1).[†] No intramolecular secondary F⋯Mo interactions were identified by QTAIM calculations.[†] An analysis of the bonding orbitals reveals that the MoO₂ unit in the anion of **1** (Fig. S6)[†] displays a bonding pattern that is qualitatively similar to that found in the neutral species MoO₂(C₆F₅)₂. This is due to the fact that the orbitals that are mainly responsible for the three M–C bonds are not involved in the MoO₂ bonding system. The calculated bond order of 2.5 for each Mo–O bond (Scheme 4c) is in keeping with the short bond length: average Mo–O 169.1(3) pm. Similar results have been obtained for the related anionic species (MoO₂X₃)[−] with X = H, Cl or CN (Fig. S5 and Table S1).[†] These simple mononuclear species are likely to associate in dimers in condensed phase, as experimentally observed in the aforementioned tungsten(vi) derivative [PPh₄]₂[(WO₂Cl₃)₂] (Scheme 1c).¹⁶ The reverse dissociation process was suggested to occur upon heating the [NMe(octyl)₃]₂[(MoO₂Cl₃)₂] salt at 200 °C in the solid state,³⁷ but poor evidence for the actual formation of mononuclear [NMe(octyl)₃][MoO₂Cl₃] was given. The C₆F₅ group is a hard organic ligand, which has been assigned an electronegativity close to that of chlorine (χ_{Cl} = 3.16 in Pauling scale).³⁸ Given this formal relationship, it is reasonable to assume that the steric bulk of the C₆F₅ groups together with the protective effect of the *ortho*-F substituents are the main factors precluding the association of [MoO₂(C₆F₅)₃][−] units into dimers. Moreover, this anion shows no tendency to associate additional ligands, since compound **1** fails to react at room temperature with sterically suited ligands, such as *t*-BuNC or MeCN. This lack of reactivity also points to a diminished acidity of the molybdenum(vi) center.

Stereochemical stability

The room temperature ¹⁹F NMR spectrum of **1** in CD₂Cl₂ solution shows two F^o signals in 2:1 relative ratio (Fig. 4a). Two sets of F^m and F^p signals with the same relative ratio are also observed (Fig. 4b). This pattern, showing the presence of two chemically inequivalent C₆F₅ groups, is in keeping with the solid-state structure (Fig. 1). One of the most characteristic features of five-coordinate compounds of both metals and non-metals is their stereochemical non-rigidity in solution.^{39,40} Low energy barriers are usually associated with the dynamic process, especially in homoleptic AX₅ compounds, as for instance, in simple PF₅ (~13 kJ·mol^{−1})⁴¹ or even in sterically crowded Sb(C₆F₅)₅ (24.4(4) kJ·mol^{−1}).⁴² Compound **1**, however, shows no sign of polytopal

rearrangement up to 150 °C in dmf solution,[†] and thus exhibits a marked stereochemical stability. A lower limit of $E_a > 83$ kJ·mol⁻¹ can be estimated for the energy barrier in this case. The absence of polytopal rearrangement in compound **1** can be assigned to the special stability attained by the (MoO₂)²⁺ unit in a *cis* disposition and its reluctance to adopt a *trans* arrangement that would be required in one of the steps in a classic Berry pseudorotation mechanism.^{**43} This kind of limitation also seems to apply to related neutral AX₂Y₃ compounds, such as Me₂PF₃ and (Me₂N)₂PF₃, or non-strained cyclic derivatives, such as (CH₂)₅PF₃.³⁹ A satisfactory simulation of the experimental spectrum is shown in Fig. S7 (see ESI for details).[†]

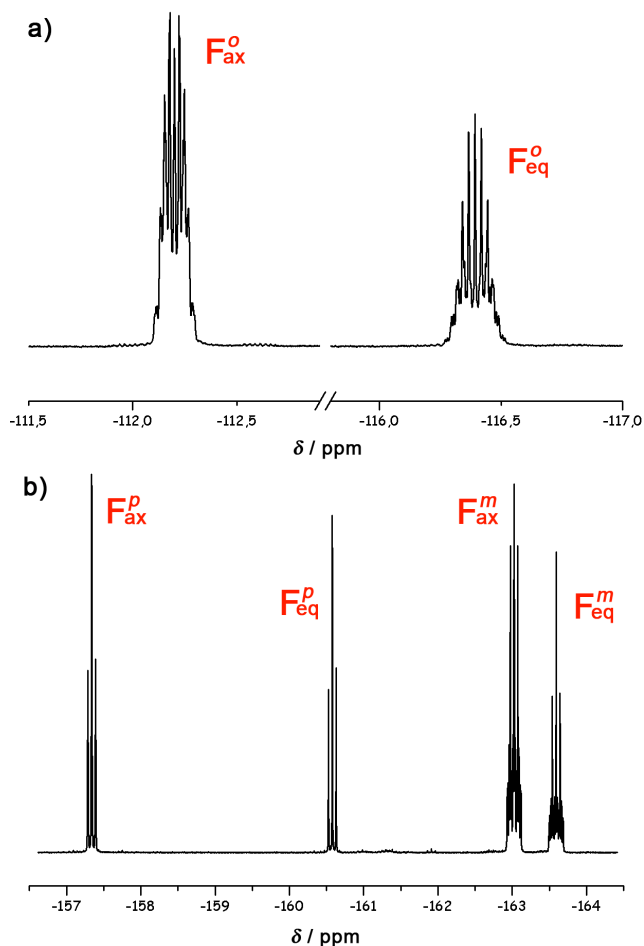
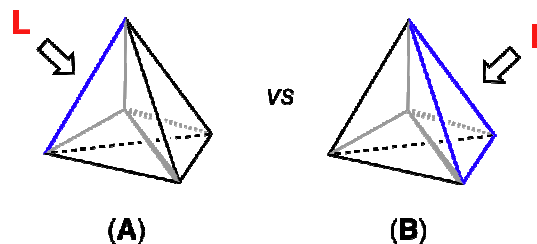


Fig. 4 ¹⁹F NMR spectrum (376.308 MHz) of compound **1** in CD₂Cl₂ solution at 293 K with higher (a) and lower (b) frequency regions depicted separately.

Conclusions

A LUMO has been identified in the series of mononuclear, tetrahedral MoO₂X₂ derivatives with X = H, Cl, CN or C₆F₅ enabling the formation of the corresponding anionic (MoO₂X₃)⁻ species. The mononuclear, five-coordinate [MoO₂(C₆F₅)₃]⁻ anion in compound **1**, which has been experimentally prepared in reasonable yield, exhibits a genuine edge-capped tetrahedral (*TE*-5) structure both in solid state (X-ray diffraction) and in solution (¹⁹F NMR spectroscopy). Similar geometries have also been found by DFT calculations to be the most energetically favored in the remaining compounds of the (MoO₂X₃)⁻ series. In view of the

congruent behavior observed in the whole series encompassing representatives of most diverse types of ligands, it can be concluded that the *TE*-5 geometry may have a wider and more prominent involvement in structural transformations than has hitherto been recognized or anticipated. Moreover, from a mechanistic point of view, the possibility of a ligand attack at the edge of a tetrahedral species (**A**) provides an interesting alternative in transition-metal chemistry to the well-known face attack (**B**), typically found, for instance, in the classic S_N2 nucleophilic substitution mechanism.⁴⁴



Experimental

General procedures and materials

Computational details are given in the ESI.[†] The reactions and manipulations were carried out under purified argon using Schlenk techniques. Solvents were dried using an MBraun SPS-800 System. The organolithium derivative LiC₆F₅ was prepared as described elsewhere.⁴⁵ The metal precursor MoCl₂O₂ was purchased (Aldrich) and used as received. Elemental analyses were carried out using a Perkin Elmer 2400 CHNS/O Series II microanalyzer. IR spectra of KBr discs were recorded on a Spectrum 100 Perkin-Elmer spectrophotometer (4000–200 cm⁻¹). Variable temperature ¹⁹F NMR spectra were recorded on a Bruker AV 400 spectrometer. Chemical shifts (δ in ppm) are given with respect to CFCl₃ as standard reference.

Synthesis of [NBu₄][MoO₂(C₆F₅)₃] (**1**)

To a dry Et₂O (40 cm³) solution of LiC₆F₅ (10.1 mmol) at -78 °C was added MoCl₂O₂ (0.5 g, 2.5 mmol) suspended in Et₂O (15 cm³) at the same temperature. The resulting suspension formed by a clear solid in purple liquor was allowed to warm slowly while stirring. At -20 °C, solid [NBu₄]Br (0.81 g, 2.52 mmol) was added and the mixture was allowed to reach room temperature. The suspension was stirred for an additional 15 h and then filtered and the filtrate was reserved for a further operation. The white solid obtained was extracted in CH₂Cl₂ (20 cm³), the extract was concentrated to dryness and the oily residue was further extracted with *i*PrOH (10 cm³) and allowed to stand for 2 days at -30 °C, after which a white solid formed. The solid was filtered, washed with *n*-hexane (3 × 3 cm³) and vacuum-dried. The main crop was obtained from the initial Et₂O filtrate by concentration and standing at 30 °C (combined weight: 1.36 g, 1.56 mmol, 62% yield). IR (KBr): ν_{max}/cm⁻¹ = 2967 (w), 2879 (w), 1504 (s), 1459 (vs), 1438 (s), 1382 (w), 1367 (w), 1348 (m), 1258 (w), 1126 (w), 1107 (w), 1061 (s), 1008 (w), 957 (vs; C–F), 913 (s; Mo–O), 883 (w; [NBu₄]⁺), 874 (w), 797 (w), 767 (w; C₆F₅; X-sensitive),⁴⁶ 738 (w; [NBu₄]⁺), 485 (w), 379 (w), 348 (w). ¹⁹F NMR (470.385 MHz, CD₂Cl₂, 293 K): δ/ppm = -112.2 (4F, F_{ax}^o), -116.4 (2F, F_{eq}^o), -157.3 (2F, F_{ax}^p), -160.6 (1F, F_{eq}^p),

–163.0 (4F, F_{ax}^m), –163.6 (2F, F_{eq}^m); this spectrum (Fig. 3) is analyzed and simulated (Fig. S7) in the ESI (Section 3).[†] MS (MALDI–, DCTB): m/z : 631 $[\text{MoO}_2(\text{C}_6\text{F}_5)_3]^-$. Elemental analysis calcd (%) for $\text{C}_{34}\text{H}_{36}\text{F}_{15}\text{NMoO}_2$: C 46.85, H 4.2, N 1.6; found: C 46.4, H 4.3, N 1.4.

X-Ray structure determination

Single crystals of $1 \cdot 1/4\text{CH}_2\text{Cl}_2$ suitable for X-ray diffraction purposes were obtained by slow diffusion of a *n*-hexane layer (20 cm^3) into a CH_2Cl_2 solution of **1** (40 mg) at -30°C . $\text{C}_{34}\text{H}_{36}\text{F}_{15}\text{MoNO}_2 \cdot 0.25\text{CH}_2\text{Cl}_2$, M_r 892.8; crystal size: $0.29 \times 0.09 \times 0.04 \text{ mm}^3$; space group $P\bar{1}$; $a = 1119.22(3)$, $b = 1295.30(4)$, $c = 1310.07(5) \text{ pm}$, $\alpha = 79.063(3)$, $\beta = 84.902(3)$, $\gamma = 83.183(3)^\circ$, $V = 1.84726(11) \text{ nm}^3$, $Z = 2$; $\rho_{\text{calc}} = 1.605 \text{ g cm}^{-3}$, $\mu = 0.499 \text{ mm}^{-1}$; graphite monochromated Mo-K α radiation ($\lambda = 71.073 \text{ pm}$); $T = 100(2) \text{ K}$; range for data collection; $4.16 \leq \theta \leq 25.50^\circ$; reflections collected/unique: 27884/6848 ($R_{\text{int}} = 0.1098$); Oxford Diffraction Xcalibur CCD diffractometer. The diffraction frames were integrated and corrected for absorption using the CrysAlis RED package.⁴⁷ Lorentz and polarization corrections were applied. The structure was solved by direct methods. Due to the only average quality of the crystals, diffraction data were in general weak. One of the *n*Bu chains of the cation was found to be disordered over two positions, which were refined each with 0.5 occupancy. Restraints in the geometry of the disordered atoms were used. Moreover, CH_2Cl_2 solvent is present near the inversion center and was refined with 0.25 occupancy. Refinement of this model against F^2 with SHELXL-97⁴⁸ converged to final residual indices of $R_1 = 0.0520$, $wR_2 = 0.0742$ [$I > 2\sigma(I)$] and $R_1 = 0.1155$, $wR_2 = 0.0812$ (all data). GoF = 0.875. CCDC 964630 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

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Notes and references

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[†] Electronic Supplementary Information (ESI) available: Theoretic calculations (DFT and QTAIM) and simulation of the experimental ^{19}F NMR spectrum of compound **1**. For ESI and crystallographic data (CCDC 964630) see DOI: 10.1039/b000000x/

[‡] The only stable iodo-derivative is formed with the heaviest metal, WO_2I_2 .^{5,6} The fluoro-derivative WO_2F_2 seems to be unstable under standard conditions,⁷ as it is also the bromo-derivative of the lighter metal, CrO_2Br_2 .⁸

§ Layered and columnar structures have been respectively found in crystals of MoO_2Br_2 ¹² and MoO_2F_2 .¹³

|| Chromyl chloride is known to react with different chloride sources giving no addition compound, but rather undergoing reduction to Cr^{V} .¹⁴

¶ A wider structural variety is found in salts of the anionic $[\text{Mo}_2\text{F}_3]^-$ oxofluorides which, depending on the cation, are associated in fluoro-bridged dimers,¹⁷ cyclic trimers,^{17c} or infinite chains of vertex-sharing $\text{Mo}_2\text{F}_2\text{F}_{2/2}$ -octahedra.¹⁸

Similar $[\text{Mo}_2\text{X}_3(\text{OH}_2)]^-$ hydrates seem to be present in concentrated HX aqueous solutions of the corresponding metal.¹⁹ On the probable existence of related species for element 106, seaborgium, see Ref. 20.

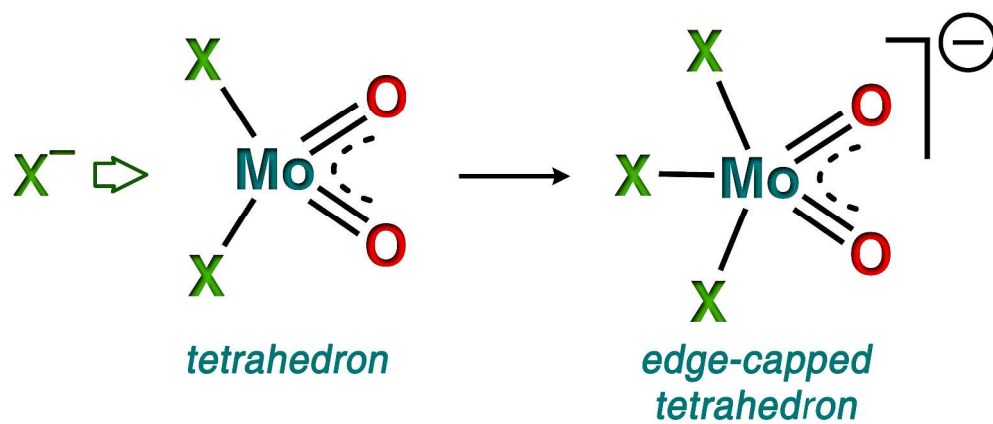
♦ We adhere the term “edge-capped tetrahedron” suggested by Alvarez and Llunell in Ref. 23c, for which we propose the TE-5 abbreviation in keeping with related standard polyhedral symbols (see Ref. 24).

⊥ An upper limit of 150°C is set by the probe manufacturer.

** Although other alternative rearrangement processes would, in principle, be possible,⁴³ it is clear that none of them works in this case, at least in the temperature range examined.

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Mononuclear $(MoO_2X_3)^{\ominus}$ compounds exhibit edge-capped tetrahedral structures, as has been theoretically calculated for $X = H, Cl$ and CN , and experimentally found for $X = C_6F_5$.

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