

Three New Polymorphic Forms of Molybdenum Pentachloride

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Abstract

Three new polymorphic modifications of molybdenum pentachloride could be obtained by solvothermal syntheses in CCl_4 and SbCl_5 as solvents. The structures have been solved by single-crystal X-ray diffraction. The already known structure of monoclinic $\alpha\text{-MoCl}_5$ ($C2/m$) is not isomorphous with $\alpha\text{-NbCl}_5$ and is better derived from the closest packing of Cl atoms of the Sm type with molybdenum occupying 1/5 of the octahedral holes. The triclinic structure of $\beta\text{-MoCl}_5$ ($P\bar{1}$) can be derived from hexagonal closest packing. The orthorhombic structure of $\gamma\text{-MoCl}_5$ ($Pnma$) and the monoclinic structure of $\delta\text{-MoCl}_5$ ($P2_1/c$) can both be derived from double-hexagonal closest packing. All four forms of MoCl_5 have in common the discrete $\text{Mo}_2\text{Cl}_{10}$ moieties built from edge-sharing double octahedra with the metal atoms displaced from the octahedron centres away from each other. The differences between the modifications lie in the different stacking sequences of the close-packed Cl-atom layers and the different occupation of the octahedral interstices. This is reflected in the group-subgroup relationships of the space groups of the closest packings and the molybdenum pentachlorides. X-ray powder diffraction shows that sublimed MoCl_5 is a mixture of all four modifications in variable amounts and probably a further unknown form.

1. Introduction

Metal and non-metal pentahalides display a great variety of crystal structures. Among the transition metal pentachlorides, -bromides and -iodides one structure type is predominant. Edge-sharing dioctahedral molecules $(MX_5)_2$ are the characteristic structural motif with many known examples, such as NbCl_5 , WCl_5 , TaI_5 or UBr_5 (Wells, 1984). All these pentahalides are volatile and monomeric in the gas phase with a trigonal bipyramidal structure (Brunvoll, Ischenko, Spiridonov & Strand, 1984). Molybdenum pentachloride also belongs to this structure family. Its structure was determined in 1959 by single-crystal diffraction (Sands & Zalkin, 1959). The crystal in this study was grown by melting MoCl_5 in a capillary and slow cooling to room temperature. Sands & Zalkin (1959) state that 'single crystals of at least three phases were obtained by this

technique' and attribute these diffraction patterns to oxychlorides. In a more recent X-ray powder diffraction study (Drobot & Pisarev, 1984) of the pentachlorides of Nb, Ta, Mo, W and Re it was stated that 'unannealed MoCl_5 is a mixture of two phases, one of which is isostructural to NbCl_5 '.

MoCl_5 is very volatile. It sublimes readily *in vacuo* at 373 K and in a stream of chlorine just above its melting point of 467 K. The black crystalline material obtained by sublimation has a powder diffraction pattern with many diffraction lines, of which only a small part can be attributed to the form investigated by Sands & Zalkin (1959; now called $\alpha\text{-MoCl}_5$).

During our attempts to synthesize sulfide or arsenide chlorides of molybdenum by solvothermal reactions, we were able to obtain several modifications of MoCl_5 in the form of single crystals. In this work their structures and integration into the $(MX_5)_2$ structural family are presented.

2. Experimental

2.1. Syntheses

CCl_4 and C_2Cl_4 were distilled over P_4O_{10} ; As and SbCl_5 were used as purchased (Aldrich). Since MoCl_5 is very rapidly hydrolysed, all manipulations were carried out in an Ar-filled glove-box with a water content of < 1 p.p.m. in a continuously regenerated atmosphere.

Molybdenum pentachloride was prepared by chlorination of powdered molybdenum metal. Impurities of MoOCl_4 and MoO_2Cl_2 were removed at 333 K *in vacuo* before MoCl_5 was freshly sublimed at 473 K.

MoOCl_4 was obtained by reaction of powdered molybdenum metal with SO_2Cl_2 at 473 K in a sealed glass ampoule inserted into an autoclave filled with pentane to achieve a counterpressure. After 3 d the autoclave was cooled and opened, the ampoule frozen with liquid nitrogen and broken under a protecting atmosphere of Ar. After thawing, the SO_2Cl_2 and all volatiles were pumped off and the product was purified by sublimation at 333 K *in vacuo*.

MoCl_4 was synthesized by reaction of powdered molybdenum metal with MoCl_5 in an evacuated glass ampoule for 2 d at 573 K and then for 5 d at 523 K. The product was purified from MoCl_5 by extraction with C_2Cl_4 .

Table 1. *Experimental details*

	β -MoCl ₅	γ -MoCl ₅	δ -MoCl ₅
Crystal data			
Chemical formula	MoCl ₅	MoCl ₅	Mo ₂ Cl ₁₀
Chemical formula weight	273.19	273.19	546.38
Cell setting	Triclinic	Orthorhombic	Monoclinic
Space group	$P\bar{1}$	$Pnma$	$P2_1/c$
a (Å)	6.716 (6)	11.700 (9)	9.4682 (7)
b (Å)	9.048 (9)	17.874 (10)	11.7496 (9)
c (Å)	6.074 (4)	6.085 (3)	12.1619 (11)
α (°)	89.19 (4)		
β (°)	118.17 (5)		108.879 (5)
γ (°)	108.85 (4)		
V (Å ³)	303.7 (5)		
Z	2	1272.5 (14)	1280.2 (2)
D_x (Mg m ⁻³)	2.988	8	4
Radiation type	Mo $K\alpha$	2.852	2.835
Wavelength (Å)	0.71073	Mo $K\alpha$	Mo $K\alpha$
No. of reflections for cell parameters	52	0.71073	0.71073
θ range (°)	7.5–12.5	200	62
μ (mm ⁻¹)	4.209	4.5–28.5	9.5–15.5
Temperature (K)	293 (2)	4.017	3.993
Crystal form	Thin plate	293 (2)	293 (2)
Crystal size (mm)	0.266 × 0.19 × 0.01	Plate	Plate
Crystal colour	Grey–black	0.23 × 0.23 × 0.11	0.24 × 0.23 × 0.11
		Black	Black
Data collection			
Diffractometer	Stoe AED-2	Stoe IPDS	Stoe AED-2
Data collection method	ω scans	–	ω – 2θ scans
Absorption correction	Numerical	Numerical	Numerical
T_{\min}	0.6818	0.4009	0.4672
T_{\max}	0.9433	0.7711	0.7407
No. of measured reflections	2144	8667	7653
No. of independent reflections	1072	1511	3755
No. of observed reflections	825	1280	2629
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	0.0266	0.0252	0.0247
θ_{max} (°)	25.05	28.20	30.03
Range of h, k, l	–7 → h → 7 –10 → k → 10 –7 → l → 7	–15 → h → 15 –23 → k → 21 –7 → l → 7	–13 → h → 12 –16 → k → 16 0 → l → 17
No. of standard reflections	3 h	–	3 h
Frequency of standard reflections	3	–	3
Intensity decay (%)	< 2	< 2	12
Refinement			
Refinement on	F^2	F^2	F^2
$R[F^2 > 2\sigma(F^2)]$	0.0220	0.0400	0.0359
$wR(F^2)$	0.0462	0.1259	0.1188
S	0.965	1.147	1.038
No. of reflections used in refinement	1072	1511	3749
No. of parameters used	55	58	110
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0179P)^2 + 0.0000P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0590P)^2 + 5.9315P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0560P)^2 + 4.1139P]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\text{max}}$	0.000	0.000	0.013
$\Delta\rho_{\text{max}}$ (e Å ⁻³)	0.491	0.798	1.460
$\Delta\rho_{\text{min}}$ (e Å ⁻³)	–0.507	–0.613	–0.856
Extinction method	None	None	SHELXL93 (Sheldrick, 1993)
Extinction coefficient	–	–	0.0045 (4)
Source of atomic scattering factors	<i>International Tables for Crystallography</i> (1992, Vol. C)	<i>International Tables for Crystallography</i> (1992, Vol. C)	<i>International Tables for Crystallography</i> (1992, Vol. C)
Computer programs			
Structure solution	SHELXS86 (Sheldrick, 1985)	SHELXS86 (Sheldrick, 1985)	SHELXS86 (Sheldrick, 1985)
Structure refinement	SHELXL93 (Sheldrick, 1993)	SHELXL93 (Sheldrick, 1993)	SHELXL93 (Sheldrick, 1993)

Na₂S was obtained from Na₂S·9H₂O by drying for 2 weeks *in vacuo* over concentrated H₂SO₄. It was heated at 973 K for 2 d in a stream of Ar to remove the last traces of water.

The magnetic properties of β-MoCl₅ were determined on a 11 mg sample of selected crystals by a Faraday susceptometer in the temperature range 20–300 K.

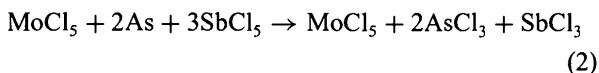
All three modifications of MoCl₅ were prepared by solvothermal reactions in glass ampoules. The ampoules (10 cm length, 1 cm diameter) were charged with the solids, dry solvent was then added and frozen with liquid N₂. After evacuation the ampoules were flame-sealed. To prevent possible explosions caused by high internal pressure the ampoules were placed in a screw-cap steel autoclave which was filled with *n*-pentane to produce a suitable high counterpressure. The screw-cap was closed with high momentum, causing the conic piston to form a seal that is gas-tight even at elevated temperatures and pressures (for details of the autoclave technique see Rabenau, 1985).

Crystals of β-MoCl₅ were grown by heating a 1:1 mixture (0.04 mol per mol of solvent) of Na₂S and MoOCl₄ for 5 d at 543 K in CCl₄ and cooling at 10 K h⁻¹ to room temperature. A black residue was also formed. The red-brown solution contained crystals of β-MoCl₅ in the form of very thin, rectangular plate-like black crystals with a metallic lustre. In transmitted light the crystals are red-brown. They are very sensitive towards any mechanical treatment and cleave easily.

Black plates of γ-MoCl₅ were obtained by heating MoCl₄ in SbCl₅ for 2 d at 573 K and cooling at 4 K h⁻¹ to room temperature.



Black crystals of δ-MoCl₅ were obtained by the reaction of MoCl₅ and As in a 1:2 ratio in SbCl₅ for 4 d at 473 K and cooling at 2 K h⁻¹ to room temperature.



2.2. Data collection and structure refinement

Owing to the sensitivity of MoCl₅ towards moist air, the single crystals were isolated in an argon-filled glove-box and fixed in sealed glass capillaries. X-ray intensity data were collected on a Stoe AED2 diffractometer for β- and δ-MoCl₅ and on a Stoe IPDS diffractometer for γ-MoCl₅. For β-MoCl₅ no symmetry higher than $\bar{1}$ was found and the space group $P\bar{1}$ was confirmed during the structure analysis. γ-MoCl₅ belongs to the orthorhombic system; the systematic extinctions (*h*0*l*: *h* + *l* = 2*n* + 1; 0*kl*: *k* = 2*n* + 1; *h*00, 0*k*0, 00*l*: *h*, *k*, *l* = 2*n* + 1) are consistent with the space groups *Pbn*2₁ and *Phnm*. Further investigation showed the centrosymmetric space group *Pbnm* is correct, which was transformed to the orthorhombic standard setting *Pnma*. Crystals of δ-MoCl₅ showed monoclinic symmetry; the systematic extinctions (*h*0*l*: *l* =

Table 2. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$U_{\text{eq}} = (1/3)\Sigma_i\Sigma_jU^{ij}a_i^*a_j^*a_i\cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
β-MoCl₅				
Mo	0.74329 (7)	0.71659 (5)	0.61106 (7)	0.01982 (11)
Cl1	0.3066 (2)	0.54412 (13)	0.5570 (2)	0.0231 (2)
Cl2	0.8656 (2)	0.64142 (15)	0.9925 (2)	0.0309 (3)
Cl3	0.4981 (2)	0.73710 (14)	0.2012 (2)	0.0313 (3)
Cl4	1.0757 (2)	0.83926 (14)	0.6408 (2)	0.0344 (3)
Cl5	0.6888 (2)	0.93418 (14)	0.7550 (2)	0.0343 (3)
γ-MoCl₅				
Mo	0.12469 (4)	0.35843 (2)	0.09031 (7)	0.0281 (2)
Cl1	0.2348 (2)	1/4	−0.0801 (3)	0.0391 (4)
Cl2	0.24509 (15)	0.34571 (10)	0.3813 (3)	0.0481 (4)
Cl3	0.00228 (14)	0.34617 (9)	−0.1982 (3)	0.0487 (4)
Cl4	0.2395 (2)	0.44145 (10)	−0.0857 (3)	0.0557 (5)
Cl5	0.0123 (2)	0.44280 (9)	0.2660 (3)	0.0554 (4)
Cl6	0.0148 (2)	1/4	0.2601 (3)	0.0374 (4)
δ-MoCl₅				
Mo1	−0.12386 (4)	0.12898 (3)	0.18541 (3)	0.02719 (12)
Mo2	0.30982 (4)	0.12463 (3)	0.29423 (3)	0.02611 (12)
Cl1	0.09130 (15)	0.01230 (11)	0.16099 (12)	0.0365 (3)
Cl2	−0.0965 (2)	0.24038 (14)	0.04016 (14)	0.0481 (3)
Cl3	−0.1001 (2)	0.01724 (14)	0.34388 (13)	0.0465 (3)
Cl4	−0.2927 (2)	0.01144 (14)	0.06188 (15)	0.0528 (4)
Cl5	−0.2890 (2)	0.24767 (14)	0.2246 (2)	0.0512 (4)
Cl6	0.0947 (2)	0.24173 (11)	0.31871 (12)	0.0369 (3)
Cl7	0.2883 (2)	0.23797 (14)	0.13689 (14)	0.0489 (4)
Cl8	0.2833 (2)	0.01448 (14)	0.44113 (13)	0.0481 (4)
Cl9	0.4740 (2)	0.00253 (14)	0.2547 (2)	0.0510 (4)
Cl10	0.4805 (2)	0.2420 (2)	0.4178 (2)	0.0552 (4)

2*n* + 1; 0*k*0, 00*l*: *k*, *l* = 2*n* + 1) are those uniquely characterizing the space group *P*2₁/*n*.

The structures were solved using the direct methods algorithms in the program *SHELXS86* (Sheldrick, 1985) and refined by full-matrix least-squares on *F*² with anisotropic displacement parameters for all atoms using the program *SHELXL93* (Sheldrick, 1993). Numerical absorption corrections were applied to all three data sets after an optimization of the crystal shapes with the aid of the program *HABITUS* (Herrendorf & Bärmighausen, 1993). Crystallographic data are summarized in Table 1. †

3. Results and discussion

3.1. Syntheses

The three new forms of MoCl₅ are obtained by crystallization from CCl₄ and SbCl₅ as solvents. All experiments proved to be reproducible and gave the pure phases in high yield. The original attempt to prepare a molybdenum oxide sulfide chloride MoOSCl₂ from MoOCl₄ and Na₂S in CCl₄ solution produced crystals of β-MoCl₅, which were also obtained by reaction of

† A list of structure factors has been deposited with the IUCr (Reference: JZ0002). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

elemental As with MoOCl₄ in the same solvent. The recrystallization of MoCl₅ from CCl₄ gives a mixture of β -MoCl₅ and at least one other crystalline MoCl₅ form, recognizable by different crystal shapes. The reaction of MoCl₄ with SbCl₅ yields black plate-like crystals of γ -MoCl₅ which were also observed when MoCl₅ is recrystallized from SbCl₅. When As is present, MoCl₅ crystallizes from SbCl₅ as δ -MoCl₅. Since As dissolves readily in SbCl₅ at elevated temperatures, the actual solvent in this reaction is a SbCl₅/SbCl₃/AsCl₃ mixture. Since all new modifications are present in sublimed MoCl₅, contamination by Sb^V is not probable. The α -form already known could not be obtained by a solvothermal crystallization, but is available from the melt as described by Sands & Zalkin (1959).

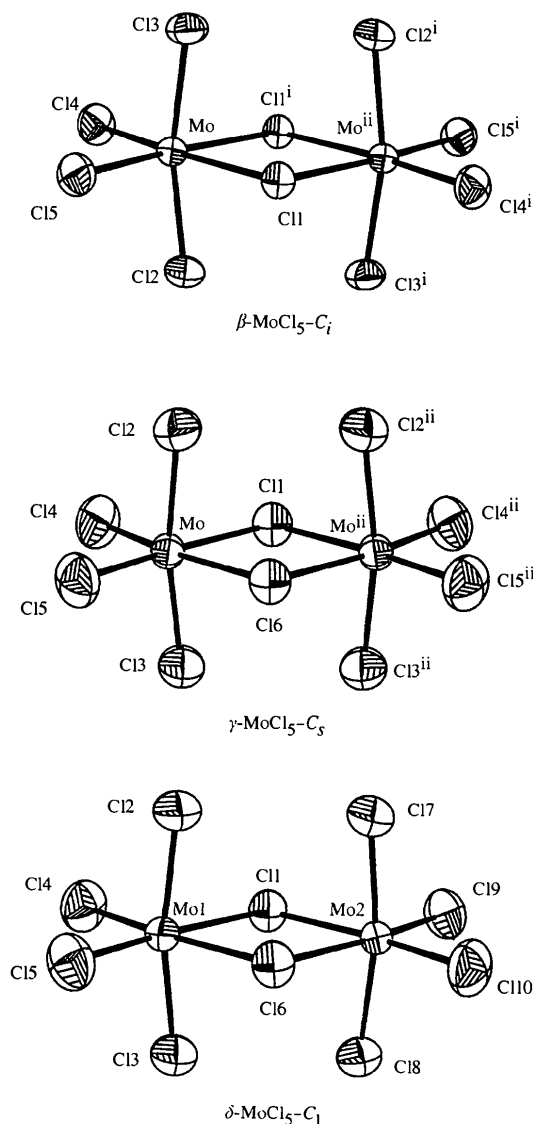


Fig. 1. Dimeric Mo₂Cl₁₀ molecules of the new MoCl₅ modifications. The ellipsoids are drawn to enclose 70% probability. Symmetry codes: (i) $1-x, 1-y, 1-z$; (ii) $x, \frac{1}{2}-y, z$.

Table 3. Selected geometric parameters ($\text{\AA},^\circ$)

β -MoCl ₅			
Mo—Cl ₄	2.244 (2)	Mo—Cl ⁱ	2.522 (3)
Mo—Cl ₂	2.246 (2)	Mo—Cl ⁱ	2.533 (3)
Mo—Cl ₅	2.250 (2)	Cl ⁱ —Mo ⁱ	2.522 (3)
Mo—Cl ₃	2.255 (2)	Mo—Mo ⁱ	3.825 (4)
Cl ₄ —Mo—Cl ₅	95.90 (8)	Cl ₅ —Mo—Cl ⁱ	91.84 (8)
Cl ₂ —Mo—Cl ₃	167.21 (4)	Cl ⁱ —Mo—Cl ⁱ	81.64 (7)
Cl ₄ —Mo—Cl ⁱ	90.63 (7)	Mo ⁱ —Cl ⁱ —Mo	98.36 (7)
γ -MoCl ₅			
Mo—Cl ₅	2.269 (2)	Mo—Cl ₃	2.276 (2)
Mo—Cl ₄	2.270 (2)	Mo—Cl ₆	2.545 (2)
Mo—Cl ₂	2.274 (2)	Mo—Cl ⁱ	2.548 (2)
		Mo—Mo ⁱⁱ	3.876 (2)
Cl ₅ —Mo—Cl ₄	97.52 (8)	Cl ₆ —Mo—Cl ⁱ	80.87 (6)
Cl ₂ —Mo—Cl ₃	168.71 (7)	Mo ⁱⁱ —Cl ⁱ —Mo	99.04 (8)
Cl ₅ —Mo—Cl ₆	91.27 (7)	Mo—Cl ₆ —Mo ⁱⁱ	99.21 (8)
Cl ₄ —Mo—Cl ⁱ	90.34 (8)		
δ -MoCl ₅			
Mo ₁ —Cl ₅	2.259 (2)	Mo ₂ —Cl ₇	2.286 (2)
Mo ₁ —Cl ₄	2.273 (2)	Mo ₂ —Cl ₉	2.279 (2)
Mo ₁ —Cl ₂	2.2796 (15)	Mo ₂ —Cl ¹⁰	2.280 (2)
Mo ₁ —Cl ₃	2.282 (2)	Mo ₂ —Cl ₈	2.2848 (15)
Mo ₁ —Cl ₆	2.5486 (14)	Mo ₂ —Cl ¹¹	2.5454 (14)
Mo ₁ —Cl ¹¹	2.5513 (14)	Mo ₂ —Cl ₆	2.5537 (14)
		Mo ₁ —Mo ₂	3.886 (1)
Cl ₅ —Mo ₁ —Cl ₄	97.34 (6)	Cl ₉ —Mo ₂ —Cl ¹⁰	97.66 (7)
Cl ₂ —Mo ₁ —Cl ₃	168.50 (6)	Cl ⁷ —Mo ₂ —Cl ₈	169.14 (6)
Cl ₅ —Mo ₁ —Cl ₆	91.14 (6)	Cl ₉ —Mo ₂ —Cl ¹¹	90.50 (5)
Cl ₄ —Mo ₁ —Cl ¹¹	90.80 (5)	Cl ¹⁰ —Mo ₂ —Cl ₆	91.11 (6)
Cl ₆ —Mo ₁ —Cl ¹¹	80.72 (4)	Cl ¹¹ —Mo ₂ —Cl ₆	80.73 (4)
Mo ₁ —Cl ¹¹ —Mo ₂	99.35 (5)	Mo ₁ —Cl ₆ —Mo ₂	99.20 (5)

Symmetry codes: (i) $1-x, 1-y, 1-z$; (ii) $\frac{x+1}{2}-y, z$.

3.2. Description of the molecular structures

The crystal structures of the known α -MoCl₅ and the three new modifications β -, γ - and δ -MoCl₅ consist of dimeric Mo₂Cl₁₀ molecules with almost mmm (D_{2h}) symmetry, composed of two MoCl₆ octahedra sharing an edge. For crystallographic reasons the maximal possible symmetry of the Mo₂Cl₁₀ molecules is $2/m$ (C_{2h}) with the two bridging Cl atoms located in the mirror plane and the two Mo atoms located on the twofold axis. In the structure of α -MoCl₅ there are two crystallographically independent molecules. Four of the 12 molecules in the unit cell show $2/m$ (C_{2h}) symmetry, the other eight molecules showing only a mirror plane (C_s). In β -MoCl₅ the Mo₂Cl₁₀ molecules show $\bar{1}$ (C_i) symmetry; the molecules of γ -MoCl₅ show m (C_s) symmetry, whereas the molecules of δ -MoCl₅ contain no elements of symmetry (C_1). Fig. 1 gives a view of the Mo₂Cl₁₀ molecules of the three new modifications. The atomic coordinates and equivalent isotropic displacement parameters are listed in Table 2. Table 3 contains selected interatomic distances and angles.

In the dimeric molecules the Mo atoms are shifted by ~ 0.2 – 0.25 \AA from the centres of the coordination

octahedra away from each other. The long Mo—Mo separation of 3.85 Å (average) indicates that there is no bonding between the d^1 -configured metal atoms. The absence of Mo—Mo interactions is also supported by the magnetic properties. In the temperature range 20–300 K β -MoCl₅ shows almost perfect paramagnetism, obeying the Curie–Weiss law with a linear dependence of $1/\chi$ versus T , a characteristic Curie–Weiss constant of $\theta = 17$ K and a magnetic moment of $1.68 \mu_B$. The spin-only value for one unpaired electron is $1.73 \mu_B$ and thus a slightly decreased magnetic moment probably caused by spin-orbit interactions is observed. The magnetic properties of a MoCl₅ sample obtained by sublimation have already been determined (Klemm & Steinberg, 1936), whereby paramagnetism with a moment of $1.55 \mu_B$ was established.

The Mo—Cl bonds to the bridging Cl_b atoms are significantly longer (on average 2.54 Å) than those to the axial Cl_a atoms (2.27 Å on average) and to the equatorial Cl_c atoms (2.26 Å on average). As a result of the distortion of the octahedral coordination environment, bond angles deviate noticeably from 90°. In particular, the Cl_b—Mo—Cl_b angle is significantly compressed (on

average 81.0°), while the Cl_c—Mo—Cl_c angles are greater than 90° (on average 96.7°).

3.3. Description of the structures as closest packings

The crystal structures of the three new MoCl₅ modifications are based on a hexagonal (h.c.p.) or double-hexagonal (d.h.c.p.) closest packing of Cl atoms, in which the Mo atoms occupy 1/5 of the octahedral holes. The structure of α -NbCl₅ can be derived from hexagonal closest packing (Sands & Zalkin, 1958). The structure is monoclinic and the triangular nets of Cl atoms are stacked along the c axis. As a consequence, the nets are not strictly congruent in the projection normal to the planes, but shifted with respect to each other. The monoclinic angle β , however, deviates with 90.6° only slightly from a right angle. The structure of α -MoCl₅ and the isomorphous WCl₅ have the same space group as and comparable lattice constants to α -NbCl₅, but have a monoclinic angle of more than 95°. The shift of the closest-packed planes is no longer negligible and the derivation from hexagonal packing is no longer possible, despite this derivation having already been postulated (Smith, Johnson & Elson, 1967). The shift due to the

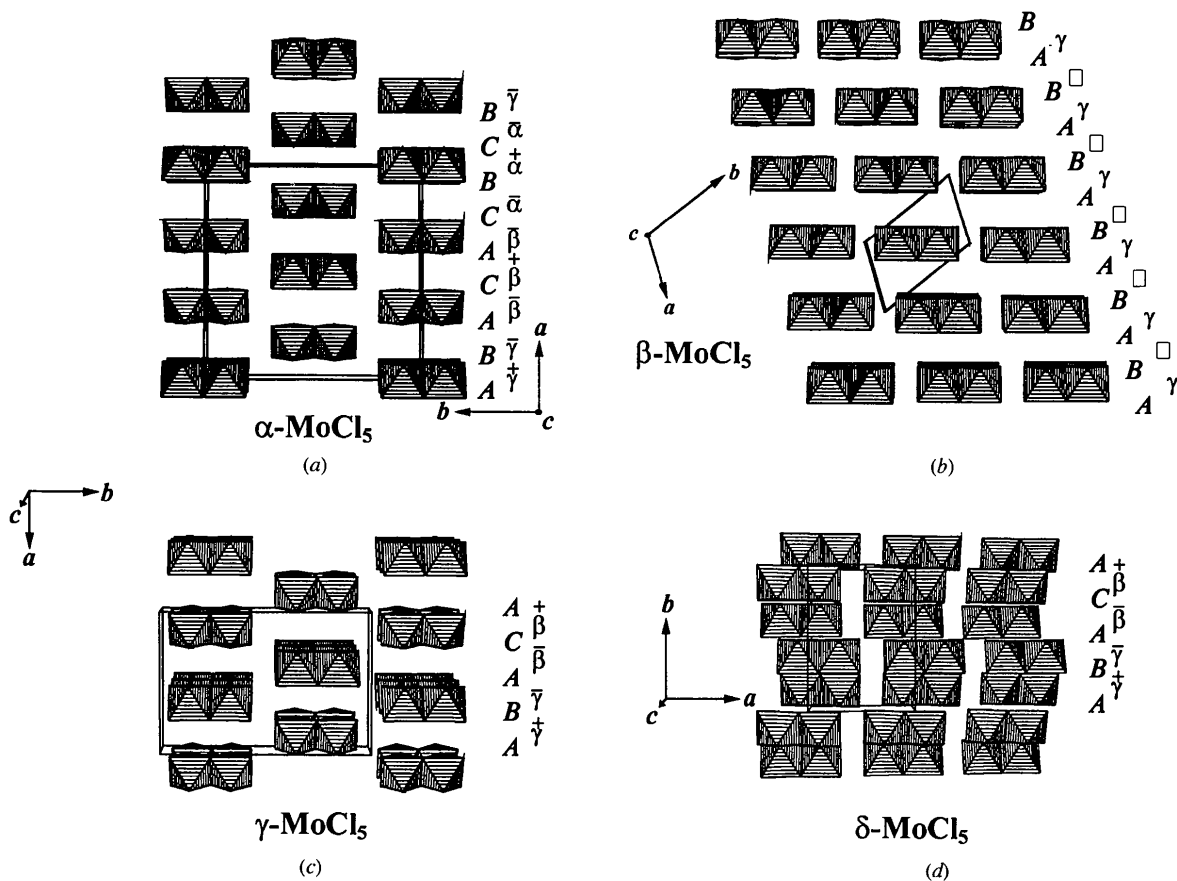


Fig. 2. View of the structures of the four known MoCl₅ modifications along the planes of the closest-packed Cl atoms. The Mo₂Cl₁₀ molecules are drawn as shaded double octahedra; the different orientations of the dioctahedral units are marked by + and -.

monoclinic angle actually causes the more complicated stacking sequence of the Sm type *ABACACBCB*,...

Müller (1978) has given an account of the structural relations of the pentahalides forming dioctahedral molecules (*MX*₅)₂ and the close-packed arrangement of halogen atoms, together with group-subgroup relationships. The derivation of the structures from closest packings implies the following requirements:

(i) The halogen atoms form hexagonal closest (h.c.p., *P6*₃/*mmc*), double-hexagonal closest (d.h.c.p., *P6*₃/*mmc*) or cubic closest (c.c.p., *F4*/*m* $\bar{3}$ *2*/*m*) packing.

(ii) Owing to the composition, the metal atoms are located in 1/5 of the octahedral interstices.

(iii) Two adjoining octahedral interstices with common edges must be occupied by the metal atoms to build up dimers of *M*₂*X*₁₀. All the surrounding octahedral interstices must be unoccupied.

Fig. 2(a) shows the structure of α -MoCl₅. The dioctahedral units have two different orientations towards the crystallographic *a* axis (marked with + and -). The stacking sequence of the layers in α -MoCl₅, taking into account the orientation of the dioctahedral units and the

occupation of the octahedral holes, is $[A\bar{\gamma}_{1/5}^+B\bar{\gamma}_{1/5}A\bar{\beta}_{1/5}C\bar{\beta}_{1/5}^+A\bar{\beta}_{1/5}C\bar{\alpha}_{1/5}^+B\bar{\alpha}_{1/5}^+C\bar{\alpha}_{1/5}B\bar{\gamma}_{1/5}^-]_2$.

The structure of β -MoCl₅ is based on a hexagonal closest packing. As Fig. 2(b) shows, only every second layer of octahedral interstices between the layers of Cl atoms is occupied by 2/5 with Mo atoms. The dioctahedral units all have the same orientation, but the translation period is not attained until the fifth layer of the octahedra. Therefore, the packing sequence is $[A\bar{\gamma}_{2/5}B\bar{\alpha}]_5$. In contrast to α - and β -MoCl₅, the structures of γ - and δ -MoCl₅ are both based on double-hexagonal closest packing. The stacking sequence for γ -MoCl₅, shown in Fig. 2(c), of the layers along the crystallographic *a* axis is $[A\bar{\gamma}_{1/5}^+B\bar{\gamma}_{1/5}A\bar{\beta}_{1/5}C\bar{\beta}_{1/5}^-]$. Fig. 2(d) shows the packing of δ -MoCl₅. The layers are stacked along the crystallographic *b* axis with the analogous sequence $[A\bar{\gamma}_{1/5}^+B\bar{\gamma}_{1/5}A\bar{\beta}_{1/5}C\bar{\beta}_{1/5}^-]$.

3.4. Group-subgroup relationships

The close relationships between the closest packing and the structures of the four MoCl₅ modifications are

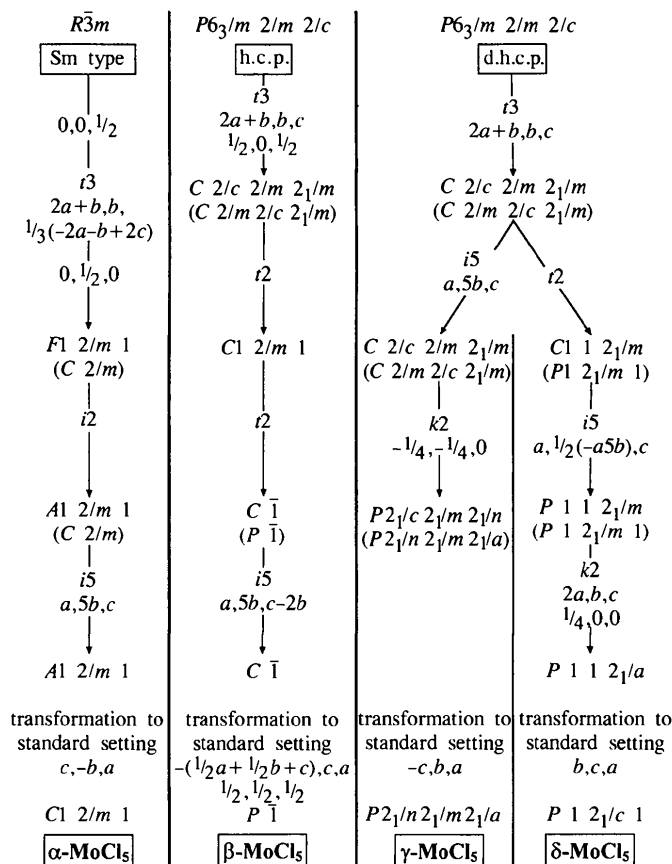


Fig. 3. Symmetry relations between the structures of the four MoCl₅ modifications and the closest packing depicted as a supergroup-subgroup family tree. The conventional settings of the unconventional space groups are given in parentheses.

Table 4. Comparison of the known pentahalides containing M_2X_{10} dimers

Structure type	Pentahalides	Space group	Molecular symmetry	Closest packing	a	b	c	α	β	γ	V	Z	Ref
A	α -MoCl ₅	C2/m	2/m,m	Sm type	1731	1781	609.9	90	95.7	90	1864.8	12	(a)
A	WCl ₅	C2/m	2/m,m	Sm type	1743.8	1770.6	606.3	90	95.51	90	1863.3	12	(b)
B	α -NbCl ₅	C2/m	2/m,m	h.c.p.	1830	1796	588.8	90	90.60	90	1935.1	12	(c)
C	β -MoCl ₅	P1	1	h.c.p.	671.6	904.8	607.4	89.19	118.17	108.85	303.7	2	(d)
C	NbI ₅	P1	1	h.c.p.	772.0	1032.2	697.7	89.07	118.04	109.63	454.4	2	(e)
C	β -UCl ₅	P1	1	h.c.p.	707	965	635	89.1	117.36	108.54	360.4	2	(f)
C	UBr ₅	P1	1	h.c.p.	744.9	1012.7	668.6	89.3	117.6	108.9	417.5	2	(g)
D	α -NbBr ₅	Pnma	m	h.c.p.	1288.8	1869.0	614.9	90	90	90	1481.2	8	(h)
E	γ -MoCl ₅	Pnma	m	d.h.c.p.	1170.0	1787	608.5	90	90	90	1272.5	8	(d)
F	δ -MoCl ₅	P2 ₁ /c	1	d.h.c.p.	946.8	1175.0	1216.2	90	108.88	90	1280.2	8	(d)
F	ReCl ₅	P2 ₁ /c	1	d.h.c.p.	924	1154	1203	90	109.1	90	1212.1	8	(f)
G	β -NbCl ₅	P2 ₁ /n	1	c.c.p.	778.5	1020.1	807.4	90	90.6	90	641.2	4	(f)
G	α -UCl ₅	P2 ₁ /n	1	c.c.p.	799	1069	848	90	91.5	90	724.1	4	(k)
G	β -PaBr ₅	P2 ₁ /n	1	c.c.p.	838.5	1120.5	895.0	90	91.1	90	840.7	4	(l)
	β -NbBr ₅	Ccmm†	2/m	h.c.p.	644	1867	615.9	90	90	90	739.4	4	(m)
	TaI ₅	Ccmm†	2/m	h.c.p.	697	2007	661	90	90	90	924.7	4	(n)

(a) Sands & Zalkin (1959); (b) Boorman, Greenwood, Hildon & Whitfield (1967); Cotton & Rice (1978); (c) Sands & Zalkin (1958), Hönlé & von Schnering (1990); (d) this work; (e) Krebs & Sinram (1980); (f) Müller & Koltisch (1974); (g) Levy, Taylor & Wilson (1978); (h) Hönlé, Furruseh & von Schnering (1990); (i) Mucker, Smith & Johnson (1968); (j) Cotton, Kibala, Matusz & Sador (1991); (k) Smith, Johnson & Elson (1967); (l) Brown, Petcher & Smith (1969); (m) Müller & Klingelhöfer (1983); (n) Müller (1979). † Averaged orthorhombic sub-structure because of a one-dimensional disorder.

confirmed by the possibility of establishing supergroup-subgroup relations between the respective space groups (Bärnighausen, 1980).

Fig. 3 shows the family tree of the four MoCl₅ modifications. The aristotype of the supergroup-subgroup relation of α -MoCl₅ is $R\bar{3}m$. A lattice-equivalent (translationsgleich = t) symmetry reduction of index 3 leads to the monoclinic crystal system; an equivalent transition of index 5 is required for the enlargement of the unit cell. The aristotype of the three new MoCl₅ modifications is $P6_3/mmc$. The first step is a lattice-equivalent symmetry reduction of index 3 to the orthorhombic setting $C2/c2/m2_1/m$. Additionally, in all three cases there is a transition to a maximal equivalent subgroup of index 5. This enlargement of the unit cell is essential to arrive at the correct composition of MoCl₅ with one occupied octahedral void and five packing atoms. The additional symmetry reductions in the three supergroup-subgroup relations are a result of the characteristic properties of the structures of the MoCl₅ modifications, especially the different stacking sequences.

3.5. Comparison of the known pentahalides containing M_2X_{10} dimers

Table 4 gives a comparison of the known pentahalides containing M_2X_{10} dimers (M = transition element; X = Cl, Br, I), whose structures contain the closest-packed arrangements of halogen atoms. There are six types of pentahalides:

(i) Pentahalides crystallizing in the monoclinic space group $C2/m$ contain two different dioctahedral units with molecular symmetry $2/m$ and m . The structures of α -MoCl₅ and WCl₅ can be derived from the closest packing of the Sm type (structure type A), while the structure of α -NbCl₅ can be described from a hexagonal closest packing (structure type B).

(ii) Pentahalides crystallizing in the triclinic space group $P\bar{1}$ (structure type C) are based on hexagonal closest packing. The dioctahedral units have the maximal possible molecular symmetry $\bar{1}$. β -MoCl₅, NbI₅, β -UCl₅ and UBr₅ belong to this type.

(iii) Pentahalides crystallizing in an orthorhombic space group. The structures of γ -MoCl₅ and α -NbBr₅ are not isotypic, although both crystallize in the space group $Pnma$ and the dioctahedral units have the molecular symmetry m . α -NbBr₅ (structure type D) consists of hexagonal closest packing, the halogen atoms of γ -MoCl₅ (structure type E) build up double-hexagonal closest packing. The structures of β -NbBr₅ and TaI₅ are characterized by a disordered stacking of M_2X_{10} units. Neglecting distortions, both structures are isotypic to α -NbBr₅ ($Pnma$) or δ -MoCl₅ ($P2_1/c$).

(iv) Pentahalides crystallizing in the monoclinic space group $P2_1/c$ consist of double-hexagonal closest packing (structure type F). The dioctahedral units have no

crystallographic symmetry; δ -MoCl₅ is a new representative and is isotypic to ReCl₅.

(v) Pentahalides crystallizing in the monoclinic space group $P2_1/n$ contain dioctahedral units with molecular symmetry $\bar{1}$ and are based on the cubic closest packing of halogen atoms (structure type G). β -NbCl₅, α -UCl₅ and β -PaBr₅ belong to this type.

4. Conclusions

Three new polymorphs of MoCl₅ could be obtained by solvothermal reactions in the form of single crystals. Together with the already known α -MoCl₅ all four forms crystallize as dioctahedral molecules (MoCl₅)₂. All four structures can be derived from the closest-packed Cl atoms with 1/5 of the octahedral holes filled with Mo and are well integrated in the structural family of transition metal pentahalides. Guinier X-ray patterns of sublimed MoCl₅ show many reflections that cannot be explained in terms of α -MoCl₅ alone. Rather than assuming oxychloride impurities, the line-rich powder diagrams can be explained by the presence of all polymorphic forms. Only a few reflections remain unexplained. These are not caused by oxychlorides, since the structures of MoOCl₃ (Drew & Tomkins, 1970) and MoOCl₄ (Taylor & Waugh, 1980) are known. The unexplained lines probably indicate that at least one further form of MoCl₅ exists.

Temperature-dependent Guinier powder diagrams show that MoCl₅ does not undergo any crystallographically detectable phase transitions up to its melting point at 467 K. The powder patterns of MoCl₅ sublimed at 423 K, and of MoCl₅ cooled from the melt and rapidly quenched, show no differences in the number of lines, only in the intensities. This indicates that all modifications are present simultaneously, but with different relative amounts and that the free enthalpies are very similar.

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