

X-RAY DIFFRACTION STUDIES

OF SOME GROUP VIA

COMPOUNDS

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ABBREVIATIONS

X.S.C.	single crystal X-ray diffraction
X.P.	powder X-ray diffraction
Z	number of molecules per unit cell
cp	cyclopentadienyl
acac	acetylacetonate

INTRODUCTION

Of the known halides of chromium, molybdenum and tungsten only about one-third have been studied by X-ray structural techniques (see Table 1). The structures reported for these halides can be divided into three categories.

1. The two or three-dimensional lattice type is the most common. The lattice usually contains MX_6 octahedra ($M = Cr, Mo, W, X = \text{halogen}$), the overall packing of which gives the appropriate polymeric form of the halide. Examples of this type are the di- and tri-halides of chromium.
2. Molecular crystals are formed by some halides. Amongst known structures this is confined at present to the hexahalides, e.g., WCl_6 .
3. Polynuclear complexes may be formed by some of the halides, e.g. dimeric molybdenum pentachloride (Mo_2Cl_{10}).

TABLE 1

SIMPLE HALIDES OF Cr, Mo, W

II	III	IV	V	VI
CrF ₂ [★] - -	CrF ₃ [★] MoF ₃ [★] -	CrF ₄ MoF ₄ -	CrF ₅ MoF ₅ -	- MoF ₆ WF ₆
CrCl ₂ [★] MoCl ₂ WCl ₂	CrCl ₃ [★] MoCl ₃ WCl ₃	- MoCl ₄ WCl ₄	- MoCl ₅ [★] WCl ₅	- - WCl ₆ [★]
CrBr ₂ [★] MoBr ₂ WBr ₂	CrBr ₃ [★] MoBr ₃ WBr ₃	- MoBr ₄ WBr ₄	- - WBr ₅	- - -
CrI ₂ [★] MoI ₂ -	CrI ₃ [★] MoI ₃ -	- - WI ₄	- - -	- - -

- not prepared

★ X-ray structures reported

The complex halides, pseudo-halides and coordination compounds of chromium, molybdenum and tungsten have a variety of structures including some which have become classical, e.g., the binuclear $(W_2Cl_9)^{3-}$ complex ion and the polynuclear $(Mo_6Cl_8)^{4+}$ group.

As will be seen later, further structural studies are needed in this field of chromium, molybdenum and tungsten chemistry. This is particularly so

- (a) to fill the gaps in our knowledge of the simple halide structures
- (b) to solve bonding problems, e.g., metal-metal bonding in polynuclear complexes, and to elucidate those structural features which are at present subject to some controversy, e.g., whether the metal atom bonds to the N or S of the NCS^- group in thiocyanate complexes.

A most convenient and direct method of determining crystal structures is afforded by X-ray diffraction techniques.

X-ray Diffraction

Single Crystal Method

A crystal acts as a three-dimensional diffraction grating for X-rays, and the resulting reflection of X-rays by the crystal planes is governed by the geometry of the crystal lattice. The intensity of a reflection from a plane is proportional to F_{hkl}^2 . (F_{hkl} is a structure factor, and is a function of the positions and scattering power of the various atoms in the unit cell of a crystal. h, k, l are the Miller indices of a plane). The structure factors (F_{hkl}) have amplitude and phase. The amplitudes can be directly obtained from the measured intensities, but these do not enable the phases of the structure factors to be calculated. To overcome this difficulty:

- (i) A trial structure is postulated, and the atomic coordinates from this structure are refined by the least-squares method to give agreement with the observed structure factors.
- (ii) Alternatively, once the phases of a few of the stronger reflections are known, Fourier

synthesis can be used to give electron density maps. Atomic positions obtained from these maps are refined by further Fourier synthesis, until calculated and observed data show good agreement.

The advantage of single crystal work lies in its unambiguity, both in the initial assignment of the space group and in the final determination of the structure.

Powder Method

The diffraction of X-rays from the random array of crystallites in a powder gives rise to cones of reflected radiation, and portions of these cones can be recorded photographically. Such a "powder photograph" can be used

- (a) for identification of compounds
- (b) for the determination of unit cell dimensions of a compound
- (c) in favourable cases for structure determinations.

Such structural determinations from powder data are subject to the following limitations:-

1. Intensity data obtainable is confined to about ten to forty values and this is insufficient for a reliable structure determination. In many instances, it has been shown that, while correlation between observed and calculated data may have been reasonably good, single crystal measurements have exposed differences which are not evident from powder work.
2. Because of the lack of sufficient experimental data it is extremely difficult to establish systematic absences of crystal planes and hence the space group and symmetry. This often leads to such errors as, for example, assigning rhombohedral instead of hexagonal symmetry to a compound.

Limitations of X-ray Methods

As well as the limitations of the powder method mentioned above there are several other factors which have to be taken into account when discussing X-ray methods.

1. Very light atoms are difficult to locate because of their very small contribution to diffracted beams.
2. Equally difficult to distinguish are atoms which have about the same atomic number and hence are very similar in scattering power.
3. Ionization states of atoms in a compound cannot be calculated.

The points outlined above have been used as criteria in assessing the X-ray structural work reported in the literature on compounds examined in this thesis.

TABLE 2

STRUCTURAL DATA REPORTED FROM X-RAY STUDIES

Cr, Mo, W : OXIDATION STATES 0 AND I

Compound	Symmetry	Unit Cell	Z	Bond Distances Å	Experimental Method	Ref.	Remarks
$\text{Cr}(\text{C}_6\text{H}_6)_2$	—	—	-	C-C 1.386-1.407	X.S.C.	3	Chromium atom sandwiched between two benzene rings
$\text{Mo}_2\text{cp}_2(\text{CO})_6$	—	—	-	Mo-Mo 3.222 Mo-C (1.946 (carbonyl) (1.965 (1.969 Mo-C 2.3-2.4 (ring)	X.S.C.	6	Non-linear arrangement with Mo-Mo bond and terminal CO groups
$\text{W}_2\text{cp}_2(\text{CO})_6$	—	—	-	—	X.P.	7	Isomorphous with $\text{Mo}_2\text{cp}_2(\text{CO})_6$

Cr, Mo, W : OXIDATION STATE II

Compound	Symmetry	Unit Cell	Z	Bond Distances ^o A	Experi- mental Method	Ref.	Remarks
CrF ₂	Monoclinic	a=4.732 ^o A b=4.718 ^o A c=3.505 ^o A $\beta = 96.52^\circ$	2	Cr-F 2.43 2.01 1.98	X.S.C.	8	Distorted rutile type three- dimensional layer lattice; two short Cr-F distances
CrCl ₂	Orthorhombic	a=6.64 ^o A b=5.98 ^o A c=3.48 ^o A	2	Cr-Cl 2.40 2.91 Cr-Cr 4.806	X.S.C.	9	Distorted rutile type three- dimensional layer lattice
CrBr ₂	Monoclinic	a=7.11 ^o A b=3.64 ^o A c=6.21 ^o A $\beta = 93^\circ 52'$	2	Cr-Br 2.998 2.545	X.S.C.	10	Distorted rutile type three- dimensional "sandwich" layer lattice
CrI ₂	Monoclinic	a=7.545 ^o A b=3.929 ^o A c=7.505 ^o A $\beta = 115^\circ 31'$	2	Cr-I 2.74	X.S.C.	11	Distorted rutile type two- dimensional "sandwich" layer lattice

Cr, Mo, W : OXIDATION STATE II

Compound	Symmetry	Unit Cell	Z	Bond Distances Å	Experimental Method	Ref.	Remarks
$(\text{Mo}_6\text{Cl}_8)(\text{OH})_4(\text{H}_2\text{O})_2 \cdot 12\text{H}_2\text{O}$	Hexagonal	$a=15.15\overset{\circ}{\text{Å}}$ $c=11.02\overset{\circ}{\text{Å}}$	6	Mo-Mo 2.6 Mo-Cl 2.5 (in Mo_6Cl_8)	X.S.C.	12	Octahedra of six Mo atoms approximately face-centring a cube of Cl atoms surrounded by an octahedral $(\text{OH})_4(\text{H}_2\text{O})_2$ group
	Rhombohedral	$a=9.49\overset{\circ}{\text{Å}}$ $\alpha=105.96^\circ$	1				
$((\text{Mo}_6\text{Cl}_8)\text{Cl}_4 \cdot 2\text{H}_2\text{O})6\text{H}_2\text{O}$	Tetragonal	$a=9.06\overset{\circ}{\text{Å}}$ $c=28.04\overset{\circ}{\text{Å}}$	4	—	X.S.C.	13	Similar to Mo_6Cl_8 complex above
$(\text{NH}_4)_2(\text{Mo}_6\text{Cl}_8)\text{Cl}_6 \cdot \text{H}_2\text{O}$	Monoclinic	$a=19.33\overset{\circ}{\text{Å}}$ $b=14.93\overset{\circ}{\text{Å}}$ $c=9.16\overset{\circ}{\text{Å}}$ $\beta=115.2^\circ$	4	Mo-Mo 2.63 Mo-Cl 2.56 (in Mo_6Cl_8) Mo-Cl 2.43 (outside Mo_6Cl_8)	Radial Distribution X.P.	15	Similar to Mo_6Cl_8 complex above

Cr, Mo, W : OXIDATION STATE III

Compound	Symmetry	Unit Cell	Z	Bond Distances Å	Experimental Method	Ref.	Remarks
CrF_3	Rhombohedral	$a=5.2643\text{Å}$ $\alpha=56.56^\circ$		Cr-F 1.90	X.S.C.	16	CrF_6 octahedra sharing corners, with F in intermediate type packing
CrCl_3	Hexagonal	$a=6.02\text{Å}$ $c=17.3\text{Å}$	6	—	X.S.C.	18	CrCl_6 octahedra sharing corners, with Cl in cubic close packing.
CrBr_3	Hexagonal	$a=6.26\text{Å}$ $c=18.2\text{Å}$	—	—	X.S.C.	19	CrBr_6 octahedra sharing corners, with Br in hexagonal close packing
CrI_3	Hexagonal	$a=6.86\text{Å}$ $c=19.88\text{Å}$	—	—	X.P.	20	Isomorphous with CrCl_3
CrBrCl_2 CrICl_2 CrIBr_2	—	—	—	—	X.P.	32	Equivalent to ideal solution of CrX_3 and CrY_3 ($X=\text{I, Br}$, $Y=\text{Cl, Br}$)

Cr, Mo, W : OXIDATION STATE III

Compound	Symmetry	Unit Cell	Z	Bond Distances Å	Experimental Method	Ref.	Remarks
MoF ₃							
1. Dark pink	Cubic	a=3.8985Å	1	—	X.P.	21	ReO ₃ type structure
2. tan) black) crystals red)	Rhombohedral				X.P.	22	VF ₃ type structure
Cs ₃ Cr ₂ Cl ₉	Hexagonal	a=7.22Å ^o c=17.97Å ^o	2	Cr-Cr 3.12 Cr-Cl 2.52 (bridging) Cr-Cl 2.34 (terminal)	X.S.C.	29	Similar to K ₃ W ₂ Cl ₉ but no Cr-Cr bonding
K ₃ W ₂ Cl ₉	Hexagonal	a=7.17Å ^o c=16.25Å ^o	2	W-W 2.409 W-Cl 2.48 (bridging) W-Cl 2.40 (terminal)	X.S.C.	27	W ₂ Cl ₉ ³⁻ is dimeric, formed by sharing a face of two distorted octahedra. W-W distance suggests bonding between tungsten atoms

Cr, Mo, W : OXIDATION STATE III

Compound	Symmetry	Unit Cell	Z	Bond Distances Å	Experimental Method	Ref.	Remarks
CrOCl	Orthorhombic	$a=3.88\overset{\circ}{\text{Å}}$ $b=3.20\overset{\circ}{\text{Å}}$ $c=7.72\overset{\circ}{\text{Å}}$	2	Cr-Cr 3.04 Cr-Cl 2.32	X.S.C.	33	Cr-O-Cr layers separated by double halogen sheets
$\text{K}_3\text{Cr}(\text{NCS})_6 \cdot 4\text{H}_2\text{O}$	Trigonal	$a=14.18\overset{\circ}{\text{Å}}$ or $28.36\overset{\circ}{\text{Å}}$ $c=9.69\overset{\circ}{\text{Å}}$	3 (12)	Cr-S 2.45	X.S.C.	34	Layer structure of $\text{Cr}(\text{NCS})_6^{3-}$ octahedra and K^+ ions and H_2O molecules
$\text{C}_5\text{H}_5\text{NH}(\text{Cr}(\text{NCS})_4(\text{NH}_3)_2)$	Monoclinic	$a=15.52\overset{\circ}{\text{Å}}$ $b=7.64\overset{\circ}{\text{Å}}$ $c=14.64\overset{\circ}{\text{Å}}$ $\beta=102.4^\circ$	4	Reineckate Cr-N 1.95 N-C 1.15 C-S 1.76 Pyridinium C-C 1.40 C-N 1.35	X.S.C.	35	Cr bonded to N of SCN^- group. Cr-N-C angle 180°
$(\text{NH}_4\text{Cr}(\text{NCS})_4(\text{NH}_3)_2) \cdot \frac{2}{3}\text{H}_2\text{O}$	—	—	—	Reineckate Cr-N 1.97 N-C 1.14 C-S 1.80	X.S.C.	36	Octahedra of $(\text{Cr}(\text{NCS})_4(\text{NH}_3)_2)^-$ with random arrangement of NH_4^+ ions and water molecules. Cr-N-C angle 180°

Cr, Mo, W : OXIDATION STATE III

Compound	Symmetry	Unit Cell	Z	Bond Distances $\overset{\circ}{\text{A}}$	Experi- mental Method	Ref.	Remarks
Choline Reineckate	—	—	—	Reineckate Cr-N 1.94 N-C 1.27 C-S 1.64	X.S.C.	36	Cr bonded to N of SCN ⁻ group. C-N-C angle 155.5°
Cr(acac) ₃	Monoclinic	a=14.2 $\overset{\circ}{\text{A}}$ b=7.62 $\overset{\circ}{\text{A}}$ c=16.5 $\overset{\circ}{\text{A}}$ β = 99° 8'	4	—	X.S.C.	37	Distorted octahedral arrangement of oxygen atoms around Cr
Cr(F ₃ (acac)) ₃	—	—	—	—	X.P.	37	Isostructural with Cr(acac) ₃
Cr(F ₆ (acac)) ₃	—	—	—	—	X.P.	37	Isostructural with Cr(acac) ₃
Mo(acac) ₃	—	—	—	—	X.P.	76	Suggested structure similar to Cr(acac) ₃

Cr, Mo, W : OXIDATION STATE IV

Compound	Symmetry	Unit Cell	Z	Bond Distances Å	Experimental Method	Ref.	Remarks
K_2MoCl_6	Cubic	$a=9.860\overset{\circ}{\text{Å}}$	-	-	X.P.	40	Preliminary measurements only
Cs_2MoCl_6	Cubic	$a=10.264\overset{\circ}{\text{Å}}$			X.P.	40	
Cs_2WCl_6	Cubic	$a=10.209\overset{\circ}{\text{Å}}$			X.P.	40	
$K_4Mo(CN)_8 \cdot 2H_2O$	Orthorhombic	$a=16.55\overset{\circ}{\text{Å}}$ $b=11.70\overset{\circ}{\text{Å}}$ $c=8.68\overset{\circ}{\text{Å}}$	4	Mo-C 2.04-2.24 C-N 1.07-1.27 Mo-N 3.29	X.S.C.	41	Aggregate of K^+ , $Mo(CN)_8^{4-}$ ions and H_2O molecules with $Mo(CN)_8^{4-}$ as a dodecahedron

Cr, Mo, W : OXIDATION STATE V

Compound	Symmetry	Unit Cell	Z	Bond Distances Å	Experimental Method	Ref.	Remarks
CrF ₅	Orthorhombic	a=5.5 ⁰ Å b=7.4 ⁰ Å c=16.3 ⁰ Å	-	-	X.P.	43	Preliminary measurements only
MoCl ₅	Monoclinic	a=17.71 ⁰ Å b=17.81 ⁰ Å c=6.09 ⁰ Å β=95.4 ⁰	12	Mo-Cl (bridging) 2.53 Mo-Cl (terminal) 2.24 Mo-Mo	X.S.C.	46	Dimeric with two chlorine bridges i.e., Mo ₂ Cl ₁₀
LiMoF ₆	Rhombohedral R ₁	a=5.43 ⁰ Å α=57.1 ⁰	-	-	X.P.	47	Distorted NaCl type lattice of
LiWF ₆	Rhombohedral R ₁	a=5.45 ⁰ Å α=57.4 ⁰	-	-	X.P.	47	Li ⁺ and (MoF ₆) ⁻ ions
NaMoF ₆	Cubic C ₁	a=8.19 ⁰ Å	-	Mo-F 1.74 F-F 2.46	X.P.	51	Distorted NaCl type lattice of
NaWF ₆	Cubic C ₁	a=8.18 ⁰ Å	-		X.P.	47	Na ⁺ and (MoF ₆) ⁻ ions

Cr, Mo, W : OXIDATION STATE V

Compound	Symmetry	Unit Cell	Z	Bond Distances Å	Experimental Method	Ref.	Remarks
KMoF ₆	Tetragonal T	a=5.88Å ^o c=9.98Å ^o	-	-	X.P.	47	Caesium chloride type lattice
KWF ₆	Tetragonal T	a=5.85Å ^o c=10.08Å ^o	-	-	X.P.	47	Caesium chloride type lattice
RbMoF ₆	Rhombohedral R ₂	a=5.11Å ^o α=96.5°	-	-	X.P.	47	Caesium chloride type lattice
RbWF ₆	Rhombohedral R ₂	a=5.14Å ^o α=97.6°	-	-	X.P.	47	Caesium chloride type lattice
CsMoF ₆	Rhombohedral R ₂	a=5.29Å ^o α=96.0°	-	-	X.P.	47	Caesium chloride type lattice
CsWF ₆	Rhombohedral R ₂	a=5.31Å ^o α=95.5°	-	-	X.P.	47	Caesium chloride type lattice
TlMoF ₆	Rhombohedral R ₂	a=5.135Å ^o α=96.13°	-	-	X.P.	47	Caesium chloride type lattice

Cr, Mo, W : OXIDATION STATE VI

Compound	Symmetry	Unit Cell	Z	Bond Distances Å	Experimental Method	Ref.	Remarks
WCl ₆	Rhombohedral	a=6.58Å ^o ∠=55°0'	1			59	Molecular crystal -
	Hexagonal	a=6.008Å ^o c=16.68Å		W-Cl 2.24 Cl-Cl 3.14 3.21	X.S.C.	59	slightly deformed WCl ₆ octahedra
K ₂ WF ₈	Cubic	a=10.27Å ^o	-	-	X.P.	62	8 x 6 octahedral sets of F atoms with statistical distribution of K/W atoms suggested
RbWF ₇	Cubic	a=10.03Å ^o	-	-	X.P.	62	Similar to K ₂ WF ₈
CsWF ₇	Cubic	a=5.49Å ^o	-	-	X.P.	62	Cs and W in caesium chloride type lattice suggested

Cr, Mo, W : OXIDATION STATE VI

Compound	Symmetry	Unit Cell	Z	Bond Distances Å	Experimental Method	Ref.	Remarks
CrOF_4	Monoclinic	$a=12.3\overset{\circ}{\text{Å}}$ $b=5.4\overset{\circ}{\text{Å}}$ $c=7.3\overset{\circ}{\text{Å}}$ $\beta=104^\circ$	-	-	X.P.	65	Preliminary measurements only
KCrO_3F	Tetragonal	$a=5.46\overset{\circ}{\text{Å}}$ $c=12.89\overset{\circ}{\text{Å}}$	4	Cr-O 1.58	X.S.C.	70	Distorted scheelite structure
KCrO_3Cl	Monoclinic $P_{21/c}$	$a=7.79\overset{\circ}{\text{Å}}$ $b=7.50\overset{\circ}{\text{Å}}$ $c=7.80\overset{\circ}{\text{Å}}$ $\beta=91^\circ 20'$	4	Cr-Cl 2.16 K-Cl 3.29 3.42 3.48 Cl-Cl 3.97 4.22 Cr-O 1.53	X.S.C.	70	Distorted scheelite structure
$(\text{NH}_4)_3\text{MoO}_3\text{F}_3$	Cubic	$a=9.10\overset{\circ}{\text{Å}}$	4	Mo-F 1.9 F-F 5.3	X.S.C.	72	Face centred lattice of NH_4^+ and $\text{MoO}_3\text{F}_3^{3-}$ ions with extra two NH_4^+ at $1/3, 2/3$ of body diagonals

Cr, Mo, W : OXIDATION STATE VI

Compound	Symmetry	Unit Cell	Z	Bond Distances Å	Experimental Method	Ref.	Remarks
$\begin{matrix} \text{Na}_3 \\ \text{K}_3 \\ \text{Rb}_3 \\ \text{Cs}_3 \end{matrix} \begin{matrix}) \\) \\) \\) \end{matrix} \text{MoO}_3\text{F}_3$	Cubic	—	—	—	X.P.	74	All isomorphous with $(\text{NH}_4)_3\text{MoO}_3\text{F}_3$
NaWO_5	Cubic	$a=8.17\text{Å}$	—	—	X.P.	75	Preliminary measurements
CsWO_5	Rhombohedral	$a=5.31\text{Å}$ $\alpha=95.5^\circ$	—	—	X.P.	75	Preliminary measurements

OXIDATION STATE ZERO

The structure of the rather unusual compound dibenzene chromium ($\text{Cr}(\text{C}_6\text{H}_6)_2$) has been the subject of controversy between several workers. On the basis of X-ray diffraction powder studies Fischer and Weiss (1956)¹ suggested that ($\text{Cr}(\text{C}_6\text{H}_6)_2$) has three-fold symmetry. Jellinek (1960)² from single crystal X-ray diffraction data reported carbon atom positions and supported the previously reported D_{3d} symmetry for the molecule, with planar rings having alternating C-C bond distances of 1.439⁰Å and 1.353⁰Å.

Doubt was cast on this structural determination by Cotton et al. (1963)³ for two reasons,

- (i) the lack of published data, making it impossible to check the veracity of the reported structure;
- (ii) the fact that molecular orbital theory predicts six-fold symmetry of the benzene rings.

A carefully repeated X-ray single crystal study was carried out by Cotton et al.³ and they reported a new type of structure, namely, that $\text{Cr}(\text{C}_6\text{H}_6)_2$ consists

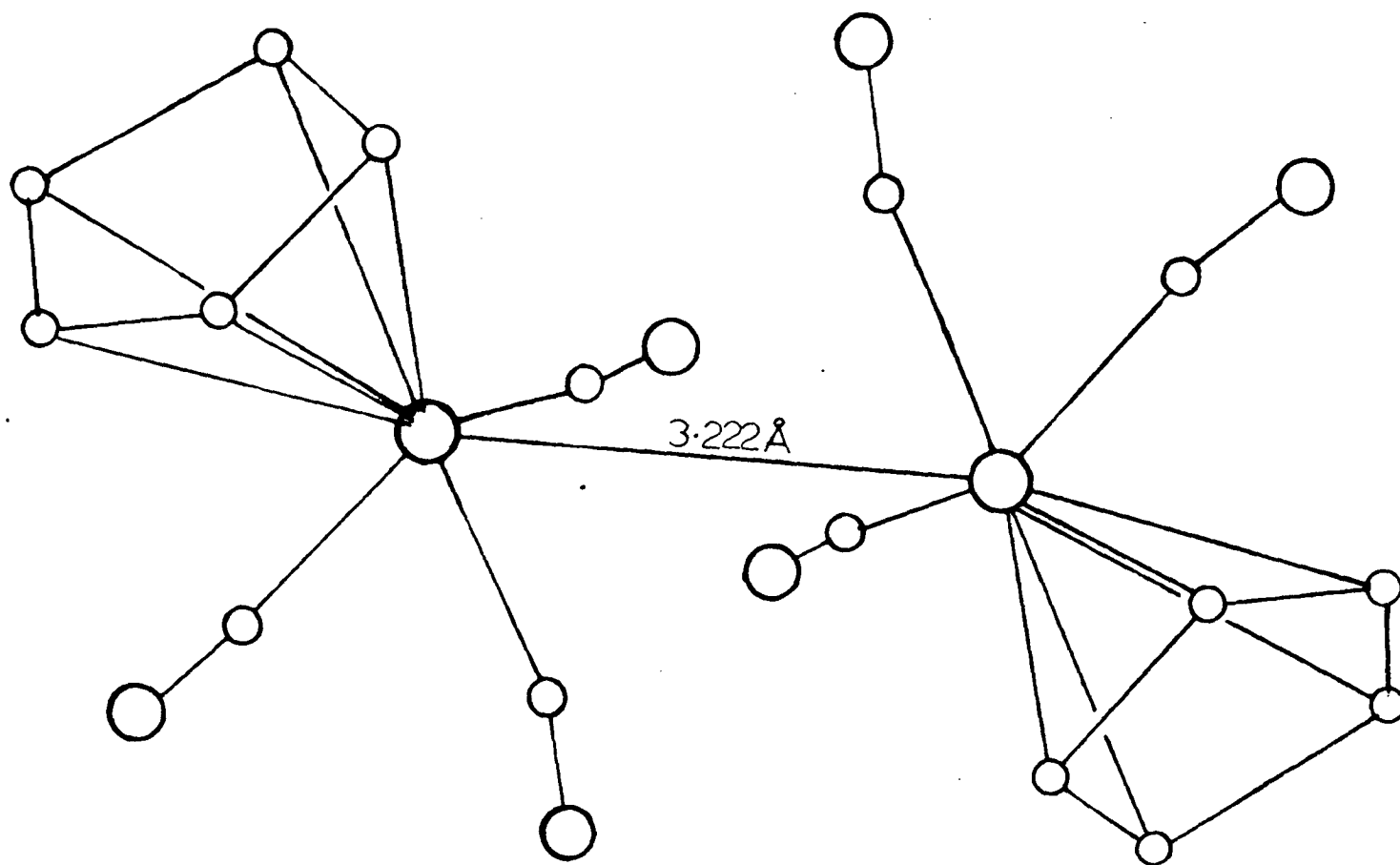
of a chromium atom at the centre of the mean plane of the carbon atoms with only very slight degradation of six-fold symmetry, such as could be readily attributed to the crystalline environment and not to any inherent tendency of the molecule to have different C-C bond lengths. The bond lengths are on the contrary very much the same (C-C $1.386\overset{\text{O}}{\text{\AA}}$ and $1.407\overset{\text{O}}{\text{\AA}}$).

Data published by these authors show good correlation between observed and calculated structure factors.

By contrast octahedral structures for $\text{Cr}(\text{CO})_6$, $\text{Mo}(\text{CO})_6$ and $\text{W}(\text{CO})_6$ have been reported by Brockway et al. (1938)⁴. These structures are based on electron diffraction measurements.

OXIDATION STATE ONE




Several univalent complexes of chromium, molybdenum and tungsten have been isolated, e.g. $(K_3Cr(CN)_5NO).H_2O$, but as yet very little structural study of these compounds has been reported. Wilkinson (1954)⁵ has proposed a structure for $Mo_2cp_2(CO)_6$ and $W_2cp_2(CO)_6$ in which the metal atoms and ring centres in the sequence $cp-M-(CO)_6-M-cp$ lie on a straight line normal to the plane of a ring of six CO groups. Wilson and Shoemaker (1956)⁶, however, have questioned this structure, and on the basis of a three dimensional X-ray diffraction study of $Mo_2cp_2(CO)_6$, have reported it to consist of a non-linear arrangement with a Mo-Mo bond and with non-bridging independently coordinated CO groups (see diagram 1). Details of this work are at present unavailable. From the similarity of their powder patterns Wilson and Shoemaker⁷ have reported $Mo_2cp_2(CO)_6$ and $W_2cp_2(CO)_6$ to be isomorphous.



- 16A -

DIAGRAM 1.

Molecular Structure of
 bis-[Cyclopentadienyl Molybdenum Tricarbonyl]

-  C
-  O
-  Mo

OXIDATION STATE TWO

HALIDES

Prior to a discussion of the structural relationship between the dihalides of chromium, a brief outline of each of the four structures will be given.

Chromium difluoride (CrF_2)

Jack and Maitland (1957)⁸ reported that CrF_2 crystallizes as a distorted rutile structure, with CrF_6 octahedra sharing corners (Cr-F distances 2.43, 2.01, 1.98⁰Å).

Chromium dichloride (CrCl_2)

According to Tracy et al. (1960)⁹ CrCl_2 crystallizes with a distorted rutile structure in which slightly distorted CrCl_6 octahedra share their shortest edge and form a densely packed linear ribbon parallel to the c-axis of the unit cell (Cr-Cl distances 2.40, 2.91⁰Å). The longer bonds link each ribbon to its four nearest neighbouring ribbons which are oriented at approximately 90° to the bond, that is, there are two bridging chlorines between the chromiums in the interacting planar chains.

Chromium dibromide (CrBr_2)

Tracy et al. (1962)¹⁰ reported CrBr_2 to have elongated CrBr_6 octahedra which share their shortest edge to form infinite planar chains and share their longer edges to form a "sandwich" type layer structure.

Chromium diiodide (CrI_2)

Tracy et al. (1962)¹¹ have also reported CrI_2 to be made up of distorted CrI_6 octahedra, which share their shortest edge to give densely packed linear ribbons parallel to the b-axis of the unit cell, and share their longer edge to form an infinite two-dimensional "sandwich" layer structure.

All four halides exhibit the basic distorted CrX_6 (X = halogen) octahedral configuration but have different packing arrangements in the crystal lattice.

Chromium difluoride differs from CrCl_2 in that

(i) CrF_2 has two different bond lengths for the short Cr-X distances, whereas CrCl_2 has only one (see table 2);

(ii) in CrF_2 the CrF_6 octahedra which share edges are not those which give maximum density to the ribbon whereas in CrCl_2 they do.

Chromium dibromide differs from CrI_2 only in the manner in which the sandwich layers are packed, CrBr_2 in three-dimensional and CrI_2 in two dimensional. The diiodide likewise differs from CrCl_2 in that CrCl_2 has a three-dimensional lattice structure (see diagram 2).

All four structure determinations were carried out using single crystal X-ray diffraction techniques with good correlation being reported, in each case, between observed and calculated structure factors.

Up to date there have been no X-ray structural studies reported for the simple dihalides of Mo and W. This is probably due to their instability and to the difficulty of crystal preparation. These compounds are of interest

(i) because their structures probably are built up from the polynuclear $(\text{Mo}_6\text{Cl}_8)^{4+}$ group known for some complex halides;

(ii) the Cr dihalides are paramagnetic whereas the Mo dihalides are diamagnetic;

(iii) the possibility that WII will form similar compounds to MoII.

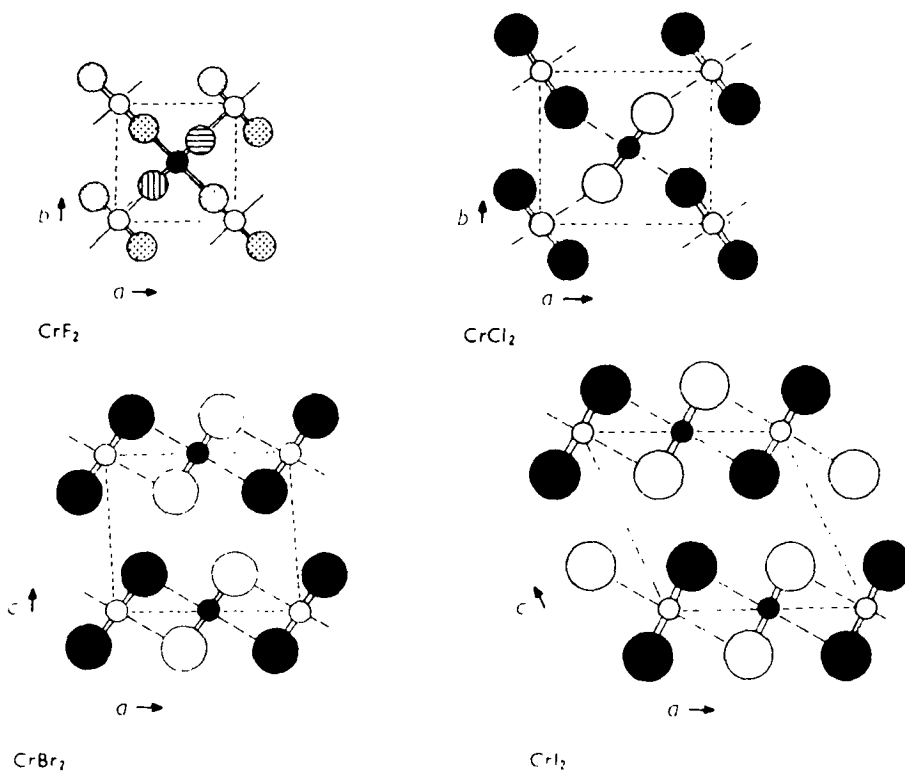


DIAGRAM 2. Small Circles Cr
Large Circles X

THE STRUCTURES OF

THE Cr^{II} HALIDES .

In an attempt to establish whether MoII formed a postulated trinuclear group $(\text{Mo}_3\text{X}_4)^{2-}$ as the basis for complex formation, the crystal structure of the compound formulated as $(\text{Mo}_3\text{Cl}_4 \cdot 2\text{H}_2\text{O})(\text{OH})_2 \cdot 6\text{H}_2\text{O}$ was studied by Brosset¹². On the basis of this X-ray study he concluded that the compound was instead $(\text{Mo}_6\text{Cl}_8)(\text{OH})_4 \cdot (\text{H}_2\text{O})_2 \cdot 12\text{H}_2\text{O}$ which he named chloromolybdenum hydroxide. The complex consists of eight Cl atoms lying at the corners of a cube, face centred with six Mo atoms, with the remaining four Cl atoms lying at the corners of a square and surrounding the $(\text{Mo}_6\text{Cl}_8)^{4+}$ group (see diagram 3).

The structural study was carried out using Laue, powder and Weissenberg X-ray techniques to obtain diffraction data which were processed by Patterson and Fourier methods, good correlation being reported between observed and calculated structure factors.

In a later work Brosset¹³ selected a complex of proposed formula $(\text{Mo}_3\text{Cl}_4 \cdot 2\text{H}_2\text{O})\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ and subjected it to a single crystal X-ray structure analysis. The conclusions he arrived at were similar to those outlined above, i.e., the compound was $(\text{Mo}_6\text{Cl}_8)(\text{Cl}_4 \cdot 2\text{H}_2\text{O})6\text{H}_2\text{O}$ -

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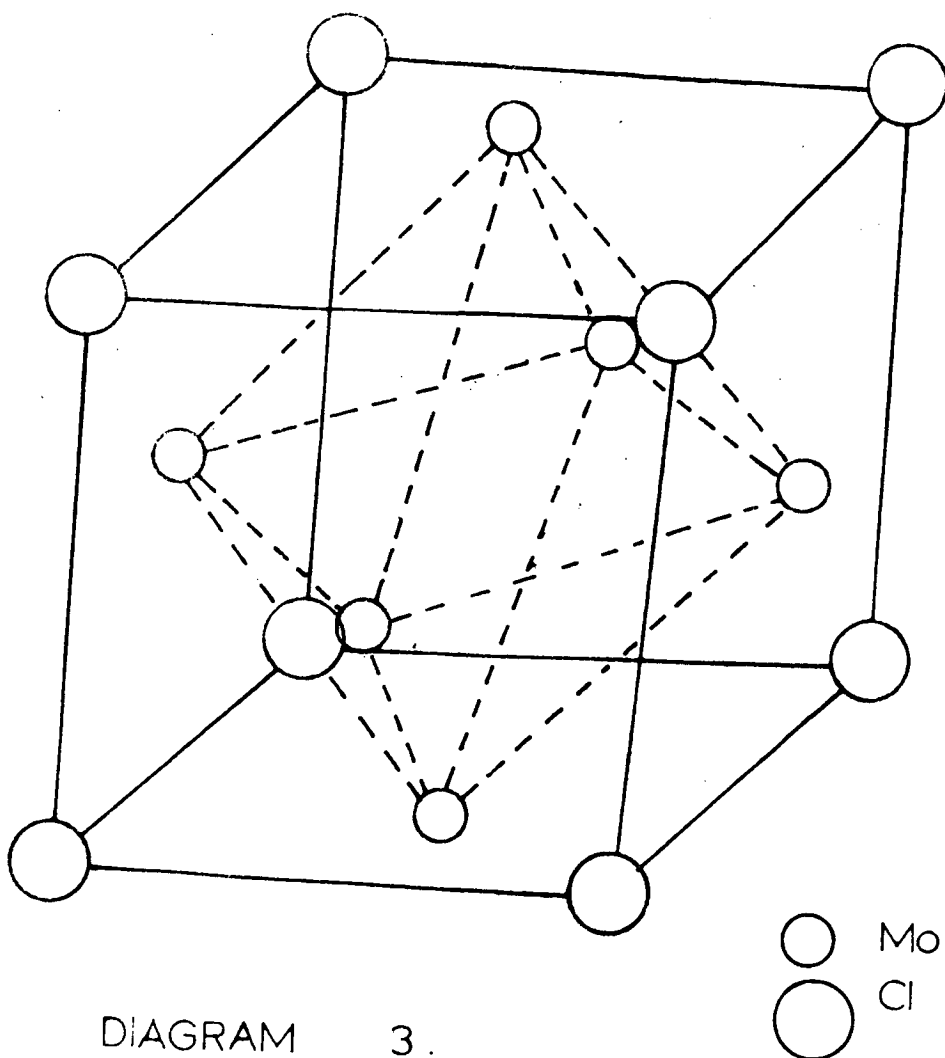


DIAGRAM 3.

THE STRUCTURE OF

THE $(\text{Mo}_6\text{Cl}_8)^{4+}$ ION.

chloromolybdenum chloride - its structure again being based on the $(\text{Mo}_6\text{Cl}_8)^{4+}$ group (see above). Again good correlation was reported between observed and calculated structure factors.

Sheldon¹⁴ reported that he had confirmed that the chloromolybdenum group normally requires octahedral coordination to give $\text{Mo}_6\text{Cl}_8\text{X}_6$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) complexes or polymeric $\text{Mo}_6\text{Cl}_8\text{X}_4$ compounds. He suggested that in these "novel type of coordination complexes" the $(\text{Mo}_6\text{Cl}_8)^{4+}$ group acts as a centre for octahedral complexes analogously to a single-atom ion. The same worker reports several similar complexes which presumably have the same basic structure as the two compounds discussed but no experimental evidence is cited to support these suggestions.

Vaughan¹⁵ reported that $(\text{NH}_4)_2\text{Mo}_6\text{Cl}_{14}\cdot\text{H}_2\text{O}$ contained the $(\text{Mo}_6\text{Cl}_8)^{4+}$ group. This structure was based on the application of the radial-distribution method to data obtained from X-ray diffraction powder techniques, there being good correlation reported between observed and calculated structure factors.

Several features of these Mo complexes require explanation

(i) the formation of these unique structures by molybdenum and not by other elements;

(ii) the nature of the bonding of the Mo and Cl atoms in the complex group $(\text{Mo}_6\text{Cl}_8)^{4+}$;

(iii) the outer chlorines are labile whereas those in the $(\text{Mo}_6\text{Cl}_8)^{4+}$ group are very stable, whereas the Mo-Cl distances are longer in the $(\text{Mo}_6\text{Cl}_8)^{4+}$ group than the distances from Mo to the outer chlorines.

OXIDATION STATE THREE

HALIDES

Chromium Trifluoride (CrF_3)

According to Knox (1960)¹⁶ CrF_3 consists of symmetric CrF_6 octahedra which share corners only to give a three-dimensional lattice.

Chromium Trichloride (CrCl_3)

Early work by Natta (1927)¹⁷, who claimed CrCl_3 to be rhombohedral and belonging to the hohohedric class, was discounted by Wooster (1930)¹⁸ who reported that CrCl_3 was hexagonal, and consisted of chlorines in positions of cubic close packing with chromiums occupying one-third of the octahedral holes formed by the chloride layers.

Chromium Tribromide (CrBr_3)

Braekken (1932)¹⁹ reported that the bromines are in positions of hexagonal close packing with the chromiums occupying two-thirds of the octahedral holes within the double layers of bromines, the different double layers being held together by Van der Waals forces only.

Chromium Triiodide (CrI_3)

Handy and Gregory (1952)²⁰ on the basis of X-ray powder studies reported that CrI_3 was isostructural with CrCl_3 .

Discussion

These four trihalides of chromium are all layer structures and are built up of CrX_6 ($\text{X} = \text{halogen}$) octahedra which by sharing corners or edges give a polymeric lattice. In CrCl_3 and CrI_3 the halogens are in positions of cubic close packing while CrBr_3 has bromines in hexagonal close packing. Chromium fluoride, on the contrary, has fluorines in an intermediate type of packing and with one-quarter of the fluorine positions vacant.

As far as the experimental structure studies are concerned, both CrF_3 and CrBr_3 have been studied using single crystal X-ray techniques with good correlation being reported between observed and calculated structure factors. Chromium chloride, on the other hand, has been the subject of controversy between two workers (see above). Apparently Natta used single crystals of a different phase. Wooster does not give in any detail the data which he used in his

structural determination of CrCl_3 and considering the doubt which arises out of this conflict, it may be necessary for a repeat single crystal X-ray diffraction study to be carried out.

Molybdenum trifluoride (MoF_3) has been studied by Gutmann and Jack (1950)²¹ who proposed a cubic rhenium oxide (ReO_3) type structure, in which the fluorines are in positions of cubic close packing with molybdenum atoms filling one-quarter of the octahedral holes between the layers, and in which one-quarter of the fluorine sites remain vacant, i.e., the structure consists of MoF_6 octahedra which share corners. This structural study was based on X-ray diffraction powder data with excellent agreement being reported between observed and calculated intensities.

La Valle et al. (1959)²² in trying to repeat the preparation of the dark pink MoF_3 ²¹ were, however, unsuccessful, their method yielding tan, black, or red crystals of MoF_3 depending on the temperature used. These, when studied by X-ray powder techniques, were shown to have a rhombohedral VF_3 type structure rather than

the previously reported cubic ReO_3 type, i.e., intermediate between cubic and hexagonal close packing.

The explanations suggested for the results obtained by Gutmann and Jack²³ were,

- (a) that more than one structural form of MoF_3 may exist or,
- (b) that the structure of MoF_3 may be sensitive to slight changes in stoichiometry or impurity content.

COMPLEX HALIDES

There are several complex halides of Mo and W which are unusual in their internal bonding. Trivalent tungsten forms some binuclear complexes, and as we have seen above divalent molybdenum exhibits a tendency to form polynuclear complexes. This phenomenon appears to be in some way connected with unusual oxidation states of the metal atoms, but as yet very little is known about the bonding within these compounds.

Brosset (1935)²⁴ on the basis of X-ray powder data established the existence of the $\text{W}_2\text{Cl}_9^{3-}$ group in

the complex halide $K_3W_2Cl_9$. This $W_2Cl_9^{3-}$ group he reports as taking the form of two slightly distorted octahedra of chlorine atoms which share one face, and in which the tungsten atoms are located centrally but closer to the plane of the shared face ($1.205\overset{\circ}{\text{\AA}}$), than to the planes of the outer faces ($1.35\overset{\circ}{\text{\AA}}$) (see diagram 4).

In a later paper Brosset (1945)²⁵ postulated on the basis of his reported W-W bond length ($2.46\overset{\circ}{\text{\AA}}$) that there is some kind of attractive force between the tungsten atoms. Pauling (1947)²⁶ in discussing this $K_3W_2Cl_9$ complex suggested that the W-W distance was consistent with a W=W double bond. The refined W-W distance ($2.409\overset{\circ}{\text{\AA}}$) reported by Watson and Waser (1958)²⁷ is even more closely in accord with strong W-W bonding and confirmation for this W-W interaction is given by the magnetic moment, $\mu = 0.55 \text{ B.M.}$ ²⁸

The three chlorines shared by the W atoms exhibit unexpectedly longer W-Cl distances ($2.48\overset{\circ}{\text{\AA}}$) than the W-Cl distances ($2.408\overset{\circ}{\text{\AA}}$) to the terminal chlorines. There does not appear as yet to be an explanation of this difference.

X-ray data from Weissenberg photographs and modern computer techniques to determine atom positions

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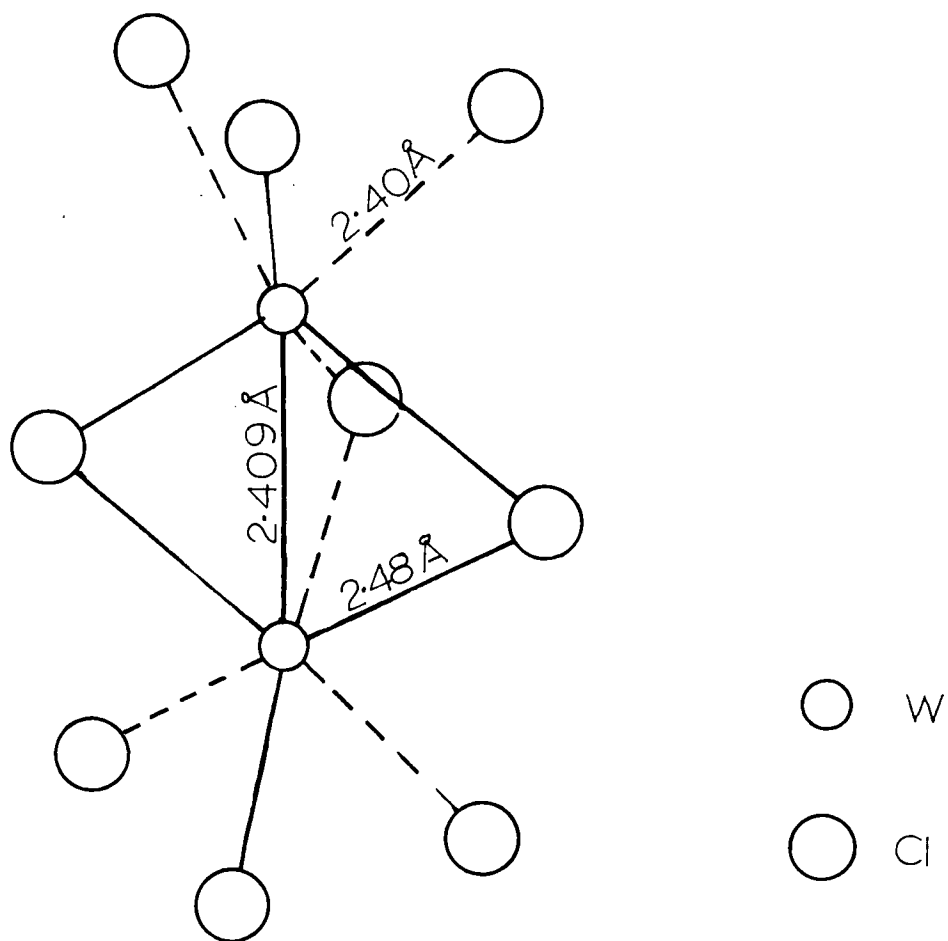


DIAGRAM 4 .

THE STRUCTURE OF

THE $W_2Cl_9^{3-}$ ION

were used in this refined study and there is reasonable correlation reported between observed and calculated structure factors.

A similar complex of CrIII, viz. $\text{Cs}_3\text{Cr}_2\text{Cl}_9$ ²⁹ has a magnetic moment corresponding to three unpaired electrons per chromium atom, indicative of a lack of interaction between the chromiums. Wessel and Ijdo (1957)²⁹ reported the crystal structure of $\text{Cs}_3\text{Cr}_2\text{Cl}_9$ to be basically similar to that of $\text{K}_3\text{W}_2\text{Cl}_9$ but with the chromium atoms shifted from the plane of the shared octahedral face towards the outer layers of chlorine atoms in the Cr_2Cl_9 ³⁻ group.

Of interest because of the possibility of trinuclear complexes of tungsten is the reported compound $\text{K}_5\text{W}_3\text{Cl}_{14}$ for which X-ray powder data obtained by Laudise and Young (1955)³⁰ show at least ten unique line spacings. There is, however, no data given and suitable corroborative structural evidence on this reported dark green crystalline compound is non-existent. In attempting to formulate a reasonable structure for this complex it is found that

there are no suitable means by which WCl_6 octahedra can share either faces, edges or corners to give the proposed $(\text{W}_3\text{Cl}_{14})^{3-}$ group.

Recent X-ray powder measurements made by König (1963)³¹ supports this, and König reports that there is no such compound as $\text{K}_5\text{W}_3\text{Cl}_{14}$ but that it is really a mixture of $\text{K}_3\text{W}_2\text{Cl}_9$ and $\text{K}_2(\text{W}(\text{OH})\text{Cl}_5)$.

MIXED HALIDES

Handy and Gregory³² have reported some mixed halides of the form CrXY_2 (X,Y = halogen). Because of the similarity of the X-ray powder patterns of these compounds to those of the parent halides, they are regarded as structurally equivalent, to the resultant expected from an ideal solution of CrX_3 and CrY_3 , with the possible exception that the halide layers may not be as closely packed.

The stoichiometric formulae for these compounds were based on the chromium content only, and then with an uncertainty of 7%.

OXY-HALIDES

The oxychloride (CrOCl) has been reported by Forsberg (1962)³³ to form Cr-O-Cr layers which are separated by double halogen sheets. This report gives a brief outline of the X-ray techniques used without reporting any experimental evidence.

PSEUDO-HALIDES

A thiocyanate complex of chromium $\text{K}_3\text{Cr}(\text{NCS})_6 \cdot 4\text{H}_2\text{O}$ has been reported by Zhdanov et al. (1953)³⁴ as being composed of $\text{Cr}(\text{NCS})_6^{3-}$ octahedra, with the Cr atom being bonded to the S atom of the NCS^- group (Cr-S distance $2.45\overset{\circ}{\text{\AA}}$). The authors quote projection methods as their means of fixing atomic positions, and postulate a layer structure of $\text{Cr}(\text{NCS})_6^{3-}$ octahedra with K^+ ions and water molecules (see diagram 5).

Some experimental intensity data have been given but no calculated values were published. There is a lack of information about the experimental methods used and the length of the a-axis has been reported to be either $14.18\overset{\circ}{\text{\AA}}$ or $28.36\overset{\circ}{\text{\AA}}$. The Cr bonding to the S of the NCS^- group is questionable because of other evidence since

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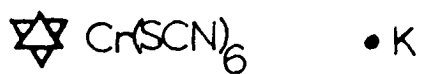
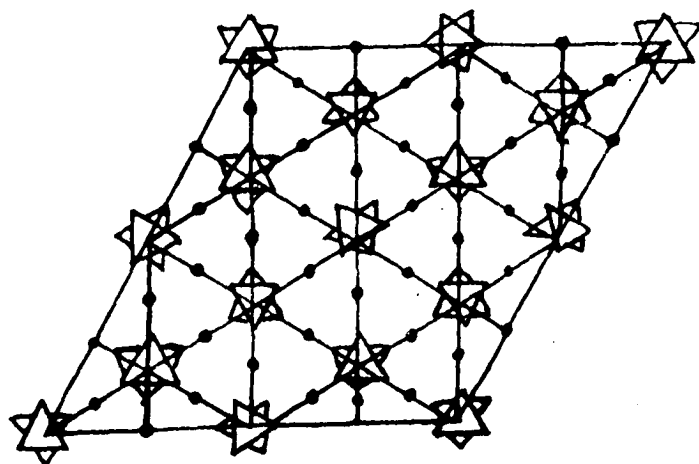


DIAGRAM 5.

PROJECTION OF $\text{K}_3\text{Cr}(\text{SCN})_6 \cdot 4\text{H}_2\text{O}$

STRUCTURE ON THE (001) PLANE .

discovered for bonding through the N of the SCN^- group (see notes on the reineckate complexes).

Structural studies reported by Takeuchi and Pepinsky³⁵ on the pyridinium complex $\text{C}_5\text{H}_5\text{NH}(\text{Cr}(\text{NCS})_4(\text{NH}_3)_2)$ show the Cr atom of the reineckate radical to be at the centre of symmetry of the molecule and bonded to the N of the SCN^- group. The pyridinium ion lies on a two-fold axis and is surrounded by twelve S atoms, four of which are coordinated to the pyridinium N with two S-N distances (3.36\AA , 3.60\AA). This single crystal X-ray structural study made use of Patterson and Fourier projections for determining atom positions, with good correlation being reported between observed and calculated structure factors. Both the reineckate salt and choline reineckate complex exhibit similar Cr-N bonding. Based on evidence from X-ray studies Takeuchi and Saito (1957)³⁶ have reported the reineckate salt $(\text{NH}_4\text{Cr}(\text{NCS})_4(\text{NH}_3)_2)^2/3\text{H}_2\text{O}$ as being composed of trans- $(\text{Cr}(\text{NCS})_4(\text{NH}_3)_2)^-$ octahedra at six corners of one-eighth of the unit cell, the other corners and body centred positions being randomly occupied by NH_4^+ ions and water molecules.

COORDINATION COMPOUNDS

The acetylacetonate complexes of CrIII and MoIII are structurally interesting in that it has been reported that $\text{Cr}(\text{acac})_3$ has a symmetric octahedral arrangement of the three oxygen atoms around the central chromium (Astbury (1926)³⁷ see diagram 6). This structural work, making use of rotating crystal and Laue techniques, together with the theory of space groups to extract atomic positions, was carried out in 1926. Like Pauling's earlier work⁷² this determination could be refined by modern X-ray methods.

Chromium trifluoroacetylacetonate ($\text{Cr}(\text{F}_3\text{acac})_3$) and chromium hexafluoroacetylacetonate ($\text{Cr}(\text{F}_6\text{acac})_3$) have been reported, on the basis of X-ray powder studies, to be isostructural with $\text{Cr}(\text{acac})_3$, with fluorines replacing three and six respectively of the hydrogen atoms on the acetylacetonate groups (see diagram 7).

Jarrett³⁸ has also reported some preliminary X-ray powder diffraction measurements on $\text{Mo}(\text{acac})_3$ and from them suggested that this complex has a similar structure to that of $\text{Cr}(\text{acac})_3$.

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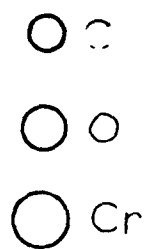
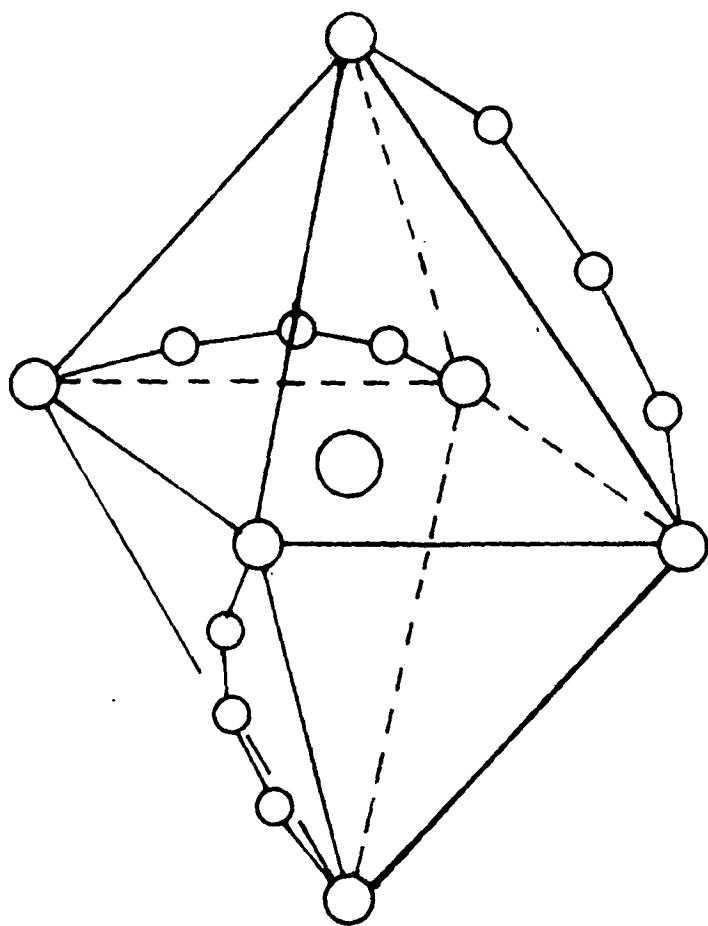
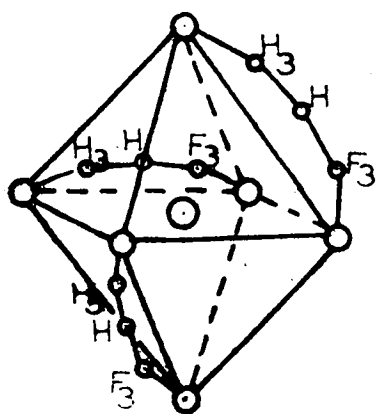


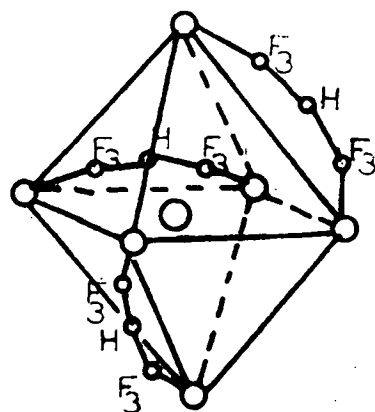
DIAGRAM 6.

THE STRUCTURE OF

tris-(ACETYLACETONATO) CHROMIUM III.



$\text{Cr}(\text{F}_3\text{acac})_3$



$\text{Cr}(\text{F}_6\text{acac})_3$

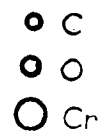


DIAGRAM 7.

OXIDATION STATE FOUR

HALIDES

On the basis of the structural knowledge of other Cr, Mo and W halides, it is suggested that the simple tetrahalides may be composed of

- (i) a tetrahedral configuration of halogen atoms around a central metal atom existing, as do the hexahalides, as molecular crystals with the tetrahedra joined together by weak forces;
- (ii) a lattice type make up of MX_6 (M = metal, X = halogen) octahedra joined by sharing edges or faces to give an effective $(MX_4)_n$ formula.

Problems involved in such studies are:-

- (a) Preparation of the crystalline compounds is difficult because they are often found mixed with halides of other metal oxidation states.
- (b) The halides are unstable in air.

Some data has been collected from X-ray single crystal and powder diffraction measurements on $MoBr_4$ ³⁹

but as yet no structural studies have been carried out. On the basis of preliminary X-ray powder measurements, McCarley and Brown⁴⁰ report that WBr_4 is isomorphous with MoBr_4 .

COMPLEX HALIDES

Complex halides of the type $\text{M}^{\text{II}}\text{MX}_6$ and $\text{M}_2^{\text{I}}\text{MX}_6$ have been isolated for Cr, Mo and W. Preliminary X-ray diffraction powder measurements on a few of these compounds have been made⁴¹.

It is probable that the structure of these complexes comprises MX_6^- octahedra in a caesium chloride or sodium chloride lattice arrangement with either M^{2+} or M^+ ions.

PSEUDO-HALIDES

Perhaps one of the most interesting compounds of MoIV is the complex cyanide $\text{K}_4\text{Mo}(\text{CN})_8 \cdot 2\text{H}_2\text{O}$. Hoard and Nordsieck (1939)⁴² described the structure as:

"the figure outlined by the vertices of two interpenetrating bisphenoids oriented in

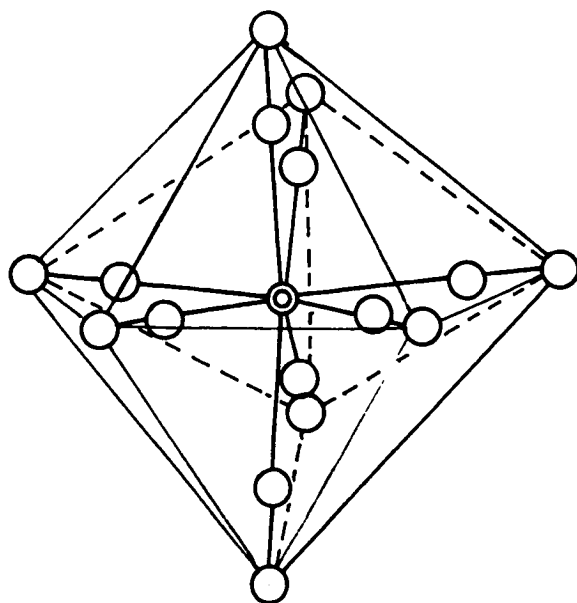
the same way as the positive and negative tetrahedra of a cube; as compared with these regular tetrahedra, one bisphenoid is considerably elongated, and the other is much flattened along the unique axis."

The crystal structure itself comprises an aggregate of K^+ and $Mo(CN)_8^{4-}$ ions and water molecules with the $Mo(CN)_8^{4-}$ group occurring as a dodecahedron (see diagram 8).

Earlier theories on the structure of $K_4Mo(CN)_8 \cdot 2H_2O$ suggested the cube or square prism as possible geometric shapes for the $Mo(CN)_8^{4-}$ group but the authors⁴² have shown the dodecahedron to be correct. Single crystal X-ray photographs in conjunction with Patterson and Fourier projections were used in the structure determination. There is no published intensity or structure factor data, although the authors claim good correlation between observed and calculated intensities.

The claim by these authors that $K_4W(CN)_8 \cdot 2H_2O$ is isostructural with $K_4Mo(CN)_8 \cdot 2H_2O$ has not as yet been confirmed by X-ray diffraction techniques.

- 35A -



⊙ Mo

○ CN^-

DIAGRAM 8.

THE STRUCTURE OF THE

IDEALIZED Mo(CN)_8 GROUP.

OXIDATION STATE FIVE

HALIDES

Edwards (1963)⁴³ in a preliminary report based on X-ray powder data has determined the unit cell dimensions of chromium pentafluoride (CrF_5). It will probably be found that the crystalline structure of chromium pentafluoride consists of CrF_6 octahedra packed in such a way as to share edges or faces to give a polymeric $(\text{CrF}_5)_n$ formula. The proposed structural work on CrF_5 by Edwards⁴⁴ will no doubt shed further light on this matter.

On the basis of electron diffraction measurements, Ewens and Lister (1938)⁴⁵ suggested a trigonal bipyramid structure for molybdenum pentachloride in the vapour state. Early electron diffraction data were subject to a basic error of theory and need to be considered with reservations⁶⁸. Sands and Zalkin in working on various pentachlorides had established much the same structure for niobium pentachloride by electron diffraction techniques. X-ray diffraction studies on the crystalline niobium compound, however, yielded an unusual dimeric ($\text{Nb}_2\text{Cl}_{10}$) structure.

Similarities observed between the X-ray powder photographs of the pentachlorides of Nb and Mo suggested that molybdenum pentachloride might itself be a dimer. Accordingly these authors⁴⁶ carried out a single crystal X-ray diffraction study of molybdenum pentachloride and verified that it does exist as $\text{Mo}_2\text{Cl}_{10}$ dimers. Each dimer consists of chlorine atoms forming two octahedra which share a common edge, with two Mo atoms occupying the centres of these octahedra and being held together by two bridging chlorine atoms (see diagram 9). Support for these chlorine bridges is given by the Mo-Cl bond distances (eight of $2.53\overset{\text{O}}{\text{\AA}}$ and two of $2.24\overset{\text{O}}{\text{\AA}}$), the two shorter bonds being due to bridging chlorines. Excellent agreement was reported between observed and calculated structure factors, and this, together with the use of single crystal X-ray diffraction work and refinement of atom positions by Fourier analysis, satisfies the criteria (see Introduction) laid down for a complete structure determination.

The corresponding tungsten pentachloride has been prepared as dark-green crystals as compared with the

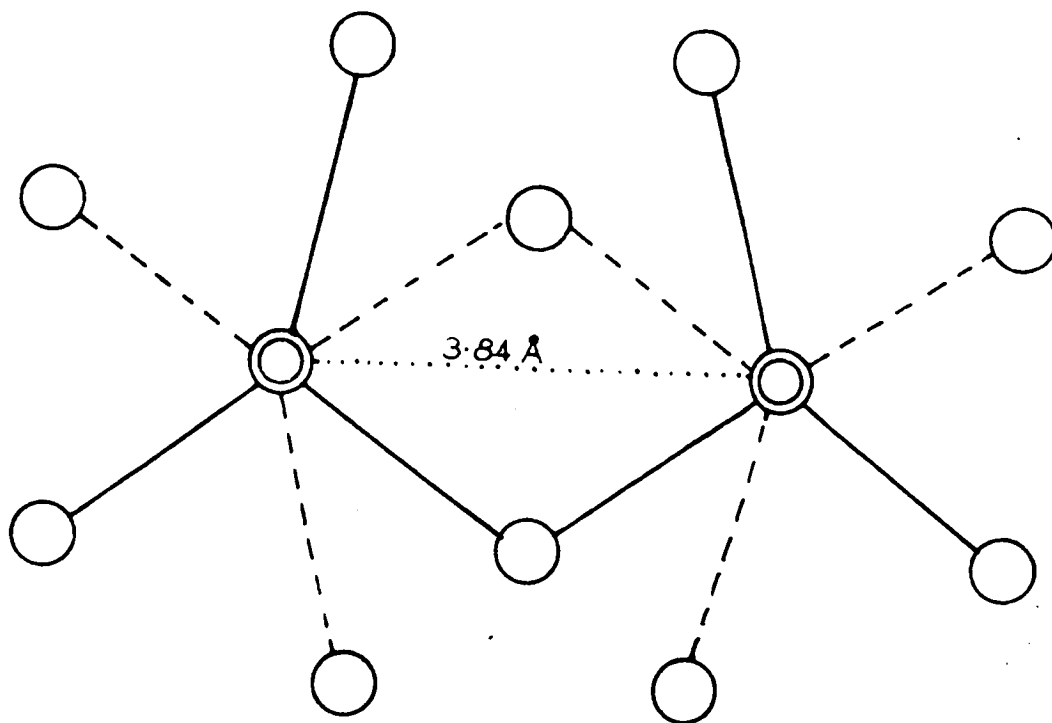


DIAGRAM 9.

Mo

Cl

THE STRUCTURE OF THE

$\text{Mo}_2\text{Cl}_{10}$ MOLECULE.

greenish-black colour of molybdenum pentachloride. Because of the close structural relationship which exists between corresponding Mo and W compounds it is probable that the tungsten and molybdenum pentachlorides will be isostructural. A comparison of the X-ray powder photographs of the two compounds would be sufficient to establish a structural relationship between them.

HALIDE COMPLEXES

The structural chemistry of the complex fluorides of MoV and WV as reported by Kemmitt, Russel and Sharp (1963)⁴⁷ follows on and incorporates the work of several other workers in this field^{48,49,50}.

The complex fluorides of general formula $A^I B^V F_6$ ($A = Li, Na, K, Rb, Cs, Te, B = Mo, W$) fall into five proposed structural types. The particular type adopted depending on the size of the ions A and B. The following is a brief summary of each of these five structural types.

R₁ is a rhombohedral and slightly distorted sodium chloride type lattice of A^+ and BF_6^- ions. The BF_6^-

ion is a regular octahedron and each A^+ is octahedrally coordinated by fluorines from six BF_6^- groups. This type of structure occurs when ions A and B are both small and comparable in size.

C₁ and C₂: Both of these structure types are cubic, having a similar sodium chloride lattice to R₁. It is difficult to find any difference between C₁ and C₂ as given by these authors and further structure study would be required to separate them.

T: This occurs as a tetragonal caesium chloride lattice structure made up of A^+ and BF_6^- ions. Each A^+ ion has eight fluorines as nearest neighbours with another four fluorines as next nearest neighbours.

R₂ is rhombohedral and related to the caesium chloride structure with the A^+ ion surrounded by twelve close packed fluorines.

The structures of the complex fluorides of MoV and WV have been deduced from evidence supplied by X-ray powder photographs, by comparison with powder data obtained for compounds of the five structural types whose structures have already been determined by single

crystal techniques. There are, however, no data given for the powder lines obtained, only unit cell dimensions being published. Granted that these show very close analogy between the postulated members of a particular structural type, more evidence both of powder and single crystal X-ray data is still required for a complete cataloguing of these compounds.

In the case of NaMoF_6 this has been done to a certain extent by Edwards and Peacock (1961)⁵¹ who have carried out a structure determination. According to them, NaMoF_6 crystallizes in a cubic (C_1) sodium chloride lattice of Na^+ and MoF_6^- ions, with the MoF_6^- ion occurring as a regular octahedron. Data for this study were obtained from X-ray powder photographs with good agreement being established between observed and calculated intensities. Powder data, despite giving apparently satisfactory results, often are insufficient for a complete structure determination (see Introduction). It is noted also that the bond distances given for Mo-F and F-F distances (see table 2) are shorter than the sum

of the corresponding ionic distances⁵², and this is reported without comment by the authors.

OXY-HALIDES

The analogy observed between NbV and MoV chlorides (see above) may be extended to their oxyhalides. Edwards (1963)⁵³ suggests that the structure of MoOCl_3 will be similar to that of niobium oxytrichloride NbOCl_3 . If this were the case, MoOCl_3 would consist of trans octahedral MoO_2Cl_4 groups linked in double chains by sharing two chlorines at an edge and sharing oxygen atoms at two opposite vertices. This has, however, not been proved by X-ray methods.

The corresponding bromide MoOBr_3 has been prepared but as in the case of MoOCl_3 no X-ray structure measurements have been attempted.

Chromium oxytrichloride (CrOCl_3) may be expected to differ somewhat from MoOCl_3 probably in the manner of packing of the molecules in the crystal lattice. This interesting group of oxyhalides could well be made the subject of structure studies.

OXY-HALIDE COMPLEXES

As shown by Allen et al. (1963)⁵⁴ MoV and WV form two types of oxyhalide complex $M_2^I(M^V OX_5)$ and $M^I(M^V OX_4)$ (M^I = univalent cation, M^V = Mo, W, X = Cl or Br). Preliminary structural studies, both spectral and magnetic, have been carried out on some of these compounds and discussed in the light of molecular orbital theory, but X-ray studies have still to be undertaken. The structure of the $M_2^I(MOX_5)$ type of oxyhalide may be made up of octahedral MOX_5^{2-} ions combined with M^+ ions in a distorted sodium chloride or caesium chloride type lattice. Once again X-ray diffraction studies would be necessary to clarify these structures.

Priest et al. (1948)⁵⁵ claimed on the basis of X-ray powder photographs that both $W_2O_5 \cdot HF \cdot H_2O$ and $W_2O_5 \cdot 2HF$ existed as cubic perovskite type crystals. Since no details of data were given this could not be checked, but if it were possible to prepare suitable crystals of the compounds it would be interesting to

pursue further studies into the structures of these unusual compounds.

In a paper by Mitchell and Williams (1962)⁵⁶ mention is made of some unpublished work of Mitchell and Prout on $\text{MoCl}_2(\text{O}^{\text{Ph}}\text{py})_3$. It is claimed that the structure of this complex is similar to that of dimeric copper acetate monohydrate in that it occurs as dimers by utilizing two chlorine bridges and direct Mo-Mo interaction. Evidence for this interaction lies in

- (i) their reported Mo-Mo bond distance of 2.8\AA (cf. Mo-Mo 2.73\AA in metallic molybdenum)⁵⁷;
- (ii) the magnetic moment $\mu = 0.42$ B.M. which is very low and suggests metal-metal interaction.

An evaluation of this proposed structure is impossible at the moment because no data is available.

Mitchell and Williams also suggest⁵⁸ on the basis of a low magnetic moment that $(\text{pyH})_2\text{MoO}_2(\text{NCS})_3$ (pyH = pyridinium) exists as dimers in the solid state, either by medium of oxide bridges (see diagram 10) or by direct spin-spin interaction. No details are, however,

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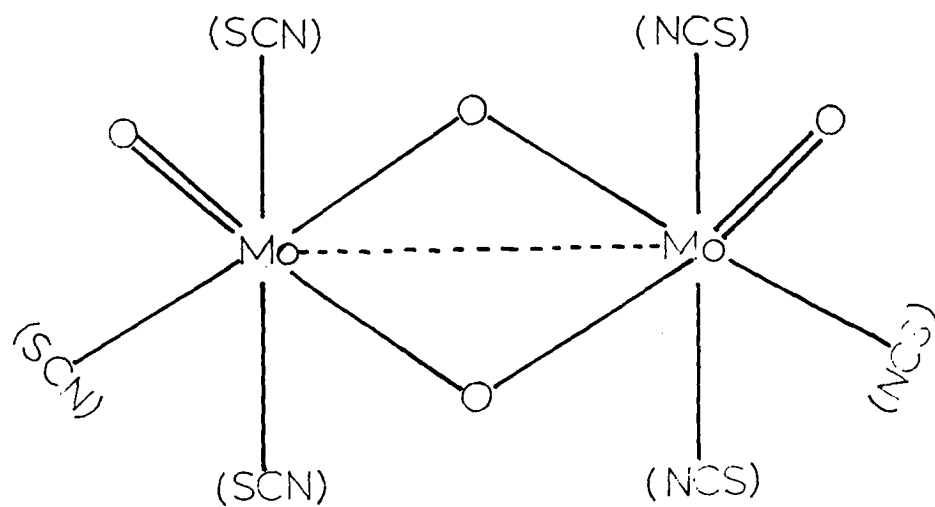
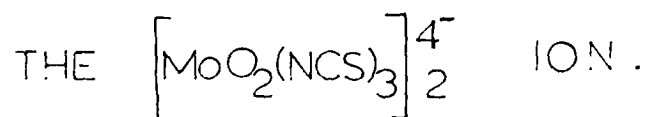


DIAGRAM 10.

THE STRUCTURE OF



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available but as in the above case of $\text{MoCl}_2(\text{O}^{\text{Ph}}\text{Py})_3$ a complete structure determination could prove very interesting.

OXIDATION STATE SIX

HALIDES

Ketelaar and van Oosterhout (1942)⁵⁹ examined WCl_6 using single crystal techniques and reported that the structure comprised a slightly distorted hexagonally close-packed arrangement of chlorine atoms with tungstens occupying one-sixth of the octahedral holes. Accordingly tungsten hexachloride is an example of a molecular crystal, i.e., it exists as discrete molecules in the solid state.

These authors give no intensity data or comparative tables of observed and calculated structure factors. This structure cannot, therefore, be accepted as completely established until such data could be studied.

It would be expected that MoF_6 and WF_6 , which have been prepared, should, in a similar fashion to WCl_6 , occur as discrete molecules in the solid state. Spectral studies by Burke et al. (1951)⁶⁰ show both MoF_6 and WF_6 to have octahedral symmetry in the vapour phase.

Electron diffraction measurements by Glauber and Schomaker⁶¹ have also supported the octahedral configuration for MoF_6 in the vapour state.

COMPLEX HALIDES

Few halide complexes of Cr, Mo and W VI have been prepared and structural information is very limited. The symmetry and unit cell dimensions of some of these compounds have been reported but complete X-ray structural work is lacking. It has been suggested by Hargreaves and Peacock⁶² that RbWF_7 and K_2WF_8 , which have very similar unit cell dimensions, exist in sets of octahedrally arranged fluorine atoms with a statistical distribution of W, and K or Rb atoms between them. In the case of CsWF_7 it has been further suggested by the same authors⁶³ that the Cs and W atoms have the same relative arrangement as in the CsCl structure but they fail to make any suggestion on the placing of the fluorine atoms. No experimental evidence has been given for these suggestions and the difficulty encountered in preparative methods has made the preparation of single crystals of these compounds impossible. Hargreaves and Peacock⁶⁴ have also reported powder diffraction data for some molybdenum complex halides and these will probably be similar in structural form to the corresponding tungsten compounds.

OXY-HALIDES

Edwards (1963)⁶⁵ in a preliminary X-ray study of CrOF_4 has reported unit cell dimensions and symmetry as a prelude to publishing a complete structure determination.

Molecular oxy-halides of the formulae CrO_2Cl_2 and MoO_2Cl_2 have been studied in the vapour state by electron diffraction by Palmer (1938)⁶⁶ and Skinner (1941)⁶⁷ respectively. Data obtained by them suggest a distorted tetrahedral arrangement. As has been seen earlier, electron diffraction measurements made about that time were subject to error⁶⁸. Because of this single crystal X-ray studies would be of interest.*

COMPLEX OXY-HALIDES

Following on optical crystallographic work by Groth (1908)⁶⁹, Helmholtz and Foster (1950)⁷⁰ reported that the complex oxy-halide KCrO_3Cl can be considered as derived from the scheelite structure (see diagram) and that it consisted of a random arrangement of CrO_3Cl^-

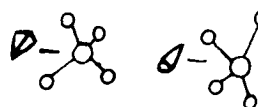
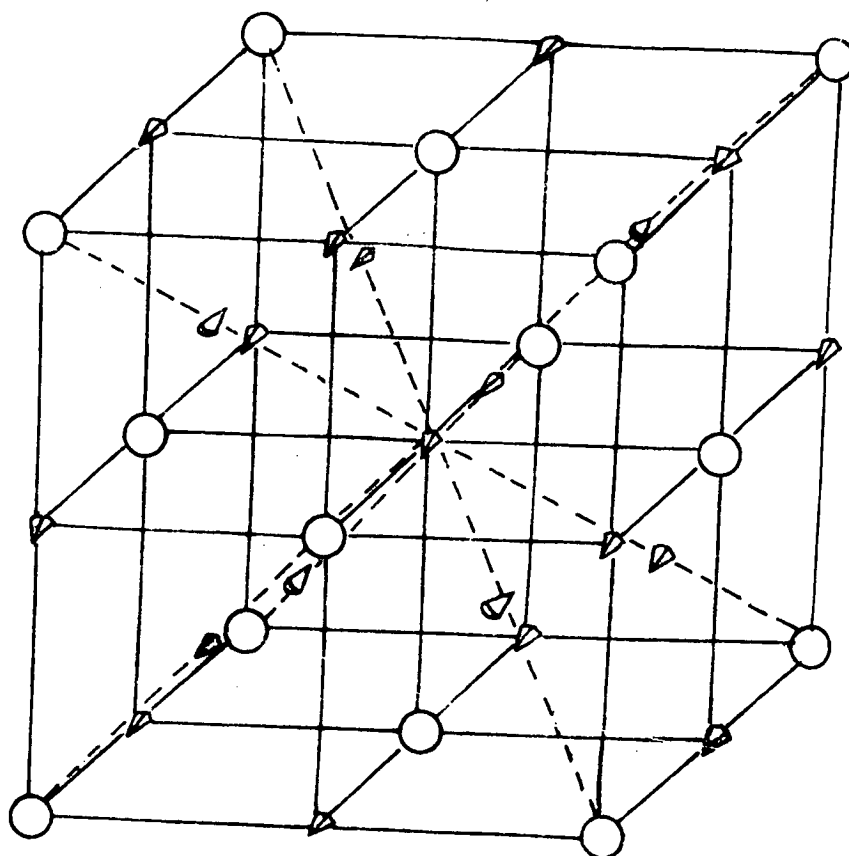
* CrO_2Cl_2 is a liquid at room temperature, hence X-ray diffraction studies would have to be carried out at a low temperature.

tetrahedra, with some deformation arising from the substitution of chlorine for oxygen. In this single crystal study both Laue and oscillation X-ray techniques were employed and although intensity data were not listed, Patterson and Fourier projections were given. The authors, however, claimed good correlation between observed and calculated structure factors.

Ketelaar and Wegerif (1938)⁷¹ demonstrated that KCrO_3F and CsCrO_3F are isomorphous, and have similar structures to that of KCrO_3Cl . Both are derived from the scheelite structure but there is less distortion caused by the presence of the smaller fluorines rather than chlorine atoms as in KCrO_3Cl . Single crystal X-ray methods used in the study of KCrO_3F fulfil the requirements for a structure determination, and although there is a lack of data in relation to intensity measurements the authors claim good correlation between observed and calculated intensities. On the basis of the similarity of their X-ray powder patterns KCrO_3F and CsCrO_3F are isomorphous. Line spacings are, however, not given.

Pauling (1924)⁷² in a classic paper on the structures of ammonium fluoro salts outlined the structure of ammonium oxyfluoromolybdate $(\text{NH}_4)_3\text{MoO}_3\text{F}_3$. This is based on a unit of four molecules in a face centred lattice with an octahedral arrangement of three oxygen and three fluorine atoms around each molybdenum with ammonium ions around them (see diagram 11). This arrangement is paralleled by that of sodium chloride where the octahedral $(\text{MoO}_3\text{F}_3)^{3-}$ ions replace Cl^- ions and NH_4^+ replace Na^+ ions, with the exception that there are two extra NH_4^+ ions at one-third and two-thirds of each of the four body diagonals of the unit cell. Pauling's structural determination was based on data obtained from Laue and powder X-ray photographs. Despite the lack of knowledge at that period about X-ray structure methods, this work appears to be extremely well executed.

Present structural methods could of course be used to verify this structure and to give bond distances, bond angles and unit cell dimensions with greater accuracy. Groth (1906)⁷³ describes $(\text{NH}_4)_3\text{WO}_3\text{F}_3$ as forming similar



ON
OH

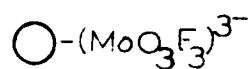


DIAGRAM 12'

THE UNIT CELL

OF (NH₄)₃MoO₃F₃ .

isotropic octahedra to $(\text{NH}_4)_3\text{MoO}_3\text{F}_3$. On the basis of this it may be assumed that the structure of $(\text{NH}_4)_3\text{WO}_3\text{F}_3$ is similar to that of $(\text{NH}_4)_3\text{MoO}_3\text{F}_3$. Of course, to verify this, X-ray powder photographs of the two compounds would need to be taken and the similarity between the two patterns established.

Schmitz-Dumont and Heckman (1952)⁷⁴ showed by the correlation between their X-ray powder patterns that the sodium, potassium, rubidium and caesium salts of the oxyfluoromolybdate complex are isomorphous with $(\text{NH}_4)_3\text{MoO}_3\text{F}_3$.

Hargreaves and Peacock (1958)⁷⁵ have, by the use of Debye X-ray photographs, reported NaWOF_5 and CsWOF_5 as to their symmetry and unit cell dimensions (see table 2). For these compounds it would perhaps be expected that there would be an octahedral configuration of an oxygen and five fluorine atoms around the central atom. The structure could then be built up in a sodium chloride or caesium chloride type structure of Na^+ or Cs^+ ions and WOF_5^- ions.

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