Investigation of the Polymorphism of Osmium Tetrachloride¹

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Depending on the method of preparation, osmium tetrachloride may be obtained in two different crystalline modifications, namely the high-temperature and the low-temperature forms. Both these species have been identified by elemental analysis and characterised by their respective x-ray powder photographs and magnetic susceptibilities. The x-ray powder data of the high-temperature form are tentatively rationalized in terms of an orthorhombic unit cell with the following dimensions: $a = 12.08 \text{ \AA}$, $b = 11.96 \text{ \AA}$ and $c = 11.68 \text{ \AA}$. From the x-ray powder diagram of the low-temperature form the cubic lattice constant $a = 9.95 \text{ \AA}$ is deduced. Reflection conditions for hkl and $h00$ are indicative of the space groups $0^6(P4_332)$ and $0^7(P4_332)$. Both compounds are paramagnetic and display low magnetic susceptibilities as a consequence of strong spin-orbit coupling. The high-temperature form exhibits the temperature-independent magnetic susceptibility $\chi_{\text{mole}} = +1080 \times 10^{-6}$ c.g.s. units, whereas for the low-temperature form the value is $\chi_{\text{mole}} = +880 \times 10^{-6}$ c.g.s. units (at 300°K). The latter susceptibility is temperature dependent. Some regularities between the uptake of chlorine by second- and third-row transition metals and the first ionization potential of the metals involved are discussed.

Octahedrally co-ordinated osmium(IV) complexes with chlorine atoms as ligands are of theoretical interest, largely as a result of their magnetic behaviour. Hence numerous studies on this class of substances have been reported in the last few years, dealing not only with bulk magnetic susceptibilities^{2a-d} but covering the main features of the respective electronic^{3a-b}, vibrational⁴ and nuclear quadrupole resonance spectra⁵. Since no such data have yet become available for osmium tetrachloride itself, some results relevant to this chloride will be presented in this paper, thus supplementing earlier investigations^{6a-e} of noble metal halides.

Up to the present time, OsCl_4 has been synthesized from its elements⁷⁻⁹, this product being the high-temperature form. The reaction is carried out either in an open reaction vessel^{7,8} or, as recently sug-

gested⁹, in a sealed tube. Only recently it was found¹⁰ that osmium metal and SO_2Cl_2 yielded the high-temperature form of OsCl_4 at 733°K . This latter procedure is the only modification of the original approach⁷ since 1910. Therefore other methods of synthesis were investigated; in particular, the reaction of OsO_4 with CCl_4 yielded the high-temperature form of OsCl_4 . Further, a new crystalline modification¹ (low-temperature form) of OsCl_4 was obtained from the reaction of OsO_4 and SOCl_2 , thus extending the number of elements in the third transition metal group which are known to form polymorphous^{11a-c} chlorides.

The two crystalline modifications of OsCl_4 were characterised by x-ray diffractometry and magnetic measurements, the following results being obtained:

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¹ Part of this work has appeared previously in communication form; see P. MACHMER, Chem. Commun. [London] **1967**, 610.

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¹¹ a) K. BRODERSEN, Angew. Chem. **73**, 437, 761 [1961]; b) K. BRODERSEN, F. MOERS, and H. G. SCHNERING, Naturwissenschaften **52**, 205 [1965]; c) D. BABEL and P. DEIGNER, Z. anorg. allg. Chem. **339**, 57 [1965].

Results of x-ray powder diffractometry

The two modifications of OsCl_4 differ in their x-ray powder patterns. The Bragg angles ϑ of the high-temperature form as prepared from OsO_4 and CCl_4 are shown in table 1.

No.	Intensity	ϑ observed	d-spacing	d-spacing (see loc. cit. ⁹)
1	10	7.7	5.7487	
2	5	10.6	4.1872	
3	5	11.2	3.9656	
4	4	12.5	3.5587	
5	6	14.7	3.0354	3.02
6	8	16.5	2.7120	2.70
7	4	17.7	2.5334	2.51
8	9	18.2	2.4661	2.46
9	3	20.1	2.2413	2.23
10	4	21.4	2.1110	2.10
11	3	21.9	2.0651	2.05
12	3	22.8	1.9877	1.98
13	2	23.7	1.9163	1.905
14	2	25.4	1.7957	1.792
15	9	26.1	1.7508	1.738
16	4	27	1.6966	1.685
17	3	28	1.6407	1.627
18	3	28.8	1.5988	1.591
19	2	32	1.4535	1.445
20	6	32.6	1.4296	1.419

Table 1. Bragg angles ϑ of the low-temperature form of OsCl_4 .

In contrast, the x-ray powder photograph of OsCl_4 as synthesized from the basic materials OsO_4 and SOCl_2 is simple and consists only of 11 lines.

No.	Intensity	ϑ observed	hkl	ϑ calculated
1	10	7.7	111	7.7
2	4	14.9	311	14.9
3	10	18.1	400	18.0
4	3	19.8	331	19.7
5	4	23.8	333	23.7
6	10	26	440	26
7	3	27.3	531	27.3
8	3	31	622	30.9
9	7	32.5	444	32.4
10	2	33.6	551	33.6
11	3	38.5	800	38.3

Table II. Bragg angles ϑ of the low-temperature form of OsCl_4 .

The x-ray powder photographs of both OsCl_4 -modifications display no lines originating from osmium metal.

Fig. 1. Schematic diagram of the x-ray patterns of the high- and the low-temperature forms of OsCl_4 .

Discussion of the x-ray data

An important feature of the x-ray powder photographs of the high-temperature form presented in this work are 4 lines in the low-angle region, which were not observed by KOLBIN⁹ and his coworkers. It is to be stressed that in the present investigation these 4 lines (those labelled with the numbers 1–4 in table I) were recorded in every high-temperature specimen of OsCl_4 irrespective of the preparation procedure involved i.e. from the elements or from OsO_4 and CCl_4 . These results undoubtedly confirm that these 4 lines are real. Moreover, they do not originate from osmium metal or osmium trichloride. Therefore they must be taken into account when the unit cell dimensions of OsCl_4 are evaluated. In particular, the x-ray data in table I can be tentatively rationalized in terms of an orthorhombic unit cell with the following dimensions: $a = 12.08 \text{ \AA}$, $b = 11.96 \text{ \AA}$ and $c = 11.68 \text{ \AA}$. However, this preliminary conclusion must await final verification by investigation of single crystals which have not yet become available.

More structural information is available on the low-temperature form. Specifically, the x-ray data given in table II yielded the cubic lattice constant $a = 9.95 \text{ \AA}$. On the basis of the recorded x-ray powder pattern the conditions for reflection were observed to be:

hkl: no conditions

h00: $h = 4n$.

These reflection conditions¹² are indicative of the space groups $\text{O}^6(\text{P}4_332)$ and $\text{O}^7(\text{P}4_132)$.

Results of the magnetic measurements

Both forms of OsCl_4 are paramagnetic. Their molar susceptibilities at 300°K , corrected for the diamagnetism of the ligands¹³, are $+1080 \times 10^{-6}$ c.g.s. units for the high-temperature form and $+880 \times 10^{-6}$ c.g.s. units for the low-temperature form. These values correspond to effective magnetic moments of 1.6 and 1.4 B.M. respectively. According to the data in table III, the paramagnetic susceptibility of the high-temperature form is temperature-independent, whereas the susceptibility of the low-temperature form varies with temperature:

Temperature [$^\circ\text{K}$]	molar susceptibilities (corrected) [$\times 10^{-6}$]
a) OsCl_4 (high-temperature form)	
373	+ 1092.4
300	+ 1080
195	+ 1099
77	+ 1083
b) OsCl_4 (low-temperature form)	
373	+ 828.4
300	+ 880
195	+ 976
77	+ 1129.3

Table III. Temperature dependence of the molar susceptibilities of the two modifications of OsCl_4 .

In this context it should be mentioned that after the communication of our data in 1967¹, COLTON and FARTHING¹⁴ published in 1968 magnetic data of the low-temperature form which differ from the values presented in table III.

In order to supplement the results of the bulk susceptibility measurements, EPR-spectroscopy was used in an attempt to investigate the high-temperature form in the solid state. However, no EPR-signal could be observed in the x-band region, either at 300°K or at 83°K .

Discussion of the magnetic results

Os^{4+} is characterised by the electron configuration $5d^4$, the 5d-orbitals being five fold degenerate in the free metal ion. However, in the solid state, the Os^{4+} ions of the crystalline compounds OsCl_4 are subjected to the influence of an electrostatic field ori-

ginating from the chloride anions. As a consequence of this perturbation and of the spin-orbit coupling, the degeneracy of the 5d-orbitals is lifted. On the basis of the space groups O^6 and O^7 it is concluded that in the low-temperature form the Os^{4+} ions are basically octahedrally co-ordinated by the chloride anions which are in turn the source of an electrostatic field of near cubic symmetry. As for the high-temperature form, a similar co-ordination of Os^{4+} by chloride anions is assumed. From grouptheoretical calculations¹⁵ it is known that under these conditions the fivefold degenerate 5d-orbitals are split into two, energetically different sets of orbitals, assigned as T_{2g} and E_g respectively. In accommodating the four electrons of Os^{4+} , the energetically favoured T_{2g} orbitals will be occupied preferentially by them, thus giving rise to a low-spin state with two unpaired electron spins. Consequently a spin-only magnetic moment of 2.83 B.M. is to be expected for osmium(IV) compounds. However, it must be pointed out that a magnetic moment of 2.83 B.M. has never yet been observed in osmium (IV) compounds. Therefore the following questions are to be raised and dealt with:

I) Why are the experimental values of the magnetic moments of the osmium tetrachlorides considerably lower than the spin-only value of 2.83 B.M.?

II) Why is the molar susceptibility of the high-temperature form greater than the molar susceptibility of the low-temperature form?

In reply the question I, the deviation from 2.83 B.M. may be attributed to at least two factors:

- The action of strong spin-orbit coupling,
- Magnetic exchange interactions between the magnetic moments of Os^{4+} ions.

In particular, the dependence of the magnetic susceptibility upon the spin-orbit coupling constant is described approximately¹⁶ by the following equation (1)

$$\chi = \frac{24 \times N \times \beta^2}{\zeta} \quad (1)$$

provided that $\zeta \gg kT$. The latter condition also accounts for the temperature independence of the

¹² International Tables for x-ray Crystallography **1**, 321 [1965], The Kynoch Press, Birmingham.

¹³ P. SELWOOD, Magnetochemistry, Second Edition, page 78, Interscience Publishers, London 1956.

¹⁴ R. COLTON and R. H. FARTHING, Australian J. Chem. **21**, 591 [1968].

¹⁵ H. A. BETHE, Ann. Physik. **3**, 133 [1929].

magnetic susceptibility if N = Avogadro's number. β = Bohr's Magnetron (0.92732×10^{-20} erg/Gauss). ζ = single-electron spin-orbit coupling parameter. From spectroscopic investigations a value of $\zeta = 4500 \text{ cm}^{-1}$ was obtained^{17a-b} which explains on the basis of equation (1) why the magnetic moments of the OsCl_4 -modifications are considerably smaller than 2.83 B.M.

Not only spin-orbit coupling but also strong magnetic interactions between adjacent Os^{4+} ions account for the reduced magnetic moment of 1.4 B.M. The latter effect has already been demonstrated¹⁸ in salts containing the anion OsCl_6^{2-} as a dope in a suitable diamagnetic host lattice. As a result of this dispersion in a diamagnetic matrix, the distances between neighbouring Os^{4+} ions become greater than in the undiluted osmium(IV) complex. Consequently, magnetic exchange interactions become less important and because of this, the magnetic moment of Os^{4+} is greater than in the pure material. A similar phenomenon can be observed in the case of the OsCl_4 -modifications.

As for question II, the dependence of the molar susceptibility of the low-temperature form upon temperature is taken as evidence of strong intermediate magnetic coupling effects which account for the lower susceptibility of this modification. Conversely, the enlarged lattice dimensions of the high-temperature form are paralleled by an increased magnetic moment and by analogy with the doping experiment¹⁸, this behaviour is interpreted in terms of reduced magnetic interactions between Os^{4+} ions which are now separated from each other by greater interatomic distances.

As has been noted previously¹⁹ for osmium(IV) complexes, the negative results of the EPR-measurements on OsCl_4 may be due to magnetic interactions causing lines which are too broad to be detected (spin-spin broadening).

Some remarks on a correlation between the different uptake of chlorine by transition metals and the first ionization potential of the metals involved

Until now no higher osmium chloride than OsCl_4 has been found to exist at 300°K . Even the reaction of OsO_4 with CCl_4 yielded only OsCl_4 , although this type of reaction is known to produce metal chlorides with the metal in its highest valence state²⁰. In this respect osmium differs sharply from rhenium which exists at 300°K as pentachloride and even as hexachloride²¹.

It is the aim of this concluding paragraph to point out that the different uptake of chlorine by these two metals can be rationalized by consideration of their first ionization potentials. Indeed, it is gratifying to see that the ability of rhenium to exist at 300°K as a hexachloride²¹ is paralleled by a lower first ionization potential (7.87 eV)²² than that of osmium, whose first ionization potential²³ is 8.7 eV. This higher value is presumably the limiting factor which prevents the existence of osmium chlorides higher than OsCl_4 (at 300°K). This correlation between the first ionization potential of the metal and the highest valence-state chloride at 300°K , as established in this particular case, is of general validity as is demonstrated by inspection of figs. 2 and 3 which represent the first ionization potentials of tungsten²², rhenium²², iridium²⁴, platinum²⁵ and gold²⁶ (and of molybdenum²², technetium²², ruthenium²², rhodium²⁷ and palladium²² respectively) as function of their highest valence-state chlorides at 300°K :

It can be seen on fig. 2 and fig. 3 that the metals existing at 300°K as high valence-state chlorides are characterised without exception by lowest ionization potentials and vice versa. This simple rule accounts also for the ability of platinum to exist as tetrachloride at 300°K .

Although there is no theoretical basis for correlating the abilities of these transition metals to

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¹⁷ a) J. S. GRIFFITH, The Theory of Transition Metal Ions, page 284, University Press, Cambridge 1961; b) B. N. FIGGIS and J. LEWIS, Progr. inorg. Chemistry **6**, 165 [1964].

¹⁸ A. D. WESTLAND and N. C. BHIWANDKER, Canad. J. Chem. **39**, 1284 [1961].

¹⁹ W. LOW, Paramagnetic Resonance in Solids, page 112, Academic Press, London-New York 1960.

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²¹ R. COLTON, Nature [London] **194**, 374 [1962].

²² V. I. VEDENEYEV, L. V. GURVICH, V. N. KONDRAT'YEV, V. A. MEDVEDEV, and YE. L. FRANKOVICH, Bond Energies-Ionization Potentials and Electron Affinities, page 152, Translated from the Russian, Arnold Publishers, London 1966.

²³ W. ALBERTSON, Physic. Rev. (2) **45**, 307 [1934].

²⁴ W. ALBERTSON, Physic. Rev. (2) **54**, 184 [1938].

²⁵ J. J. LIVINGOOD, Physic. Rev. (2) **34**, 198 [1929].

²⁶ J. R. PLATT and R. A. SAWYER, Physic. Rev. (2) **60**, 866 [1941].

²⁷ L. A. SOMMER, Z. Physik. **45**, 178 [1927].

Fig. 2. Plot of the first ionization potential of third-row transition metals as a function of their highest valence-state chlorides as existing at 300 °K.

Fig. 3. Plot of the first ionization potential of second-row transition metals as a function of their highest valence-state chlorides as existing at 300 °K.

exist as chlorides at 300 °K in which the formal valence of the metal varies between +3 and +6, with the first ionization potential of the metal, the plots have certainly an empirical value whatever their real significance may be. In the absence of any other information than the values of the first ionization potentials, it is impossible at the moment to be more precise. However, the good fit suggests that the variation of the first ionization potential in each row

parallels to a certain degree the variation of the higher ionization potentials, which themselves are not available. By this procedure the distribution of the hexachlorides among transition metals as presented in figs. 2 and 3 may be justified. Whether or not this same relationship holds for bromides and iodides of transition metals and also for actinide halides, can not be decided conclusively without more experimental data on these classes of compounds.

Experimental section

a) General description of the preparative methods applied

The black high-temperature form of $OsCl_4$, usually synthesized from its elements⁷⁻⁹, is also obtained by reacting OsO_4 with CCl_4 at 743 °K in a sealed glass tube. CCl_4 , heated to 743 °K, acts as a powerful chlorinating agent, and is aided in this respect by the high pressure generated. This reaction apparently involves transport phenomena³⁰ since the $OsCl_4$ is entirely deposited at the colder end of the reaction vessel which is subjected to a small temperature gradient (the difference in temperature between the two ends involved is approximately 70°). The reaction of OsO_4 with CCl_4 can be formulated as:

As demonstrated by x-ray diffractometry and by magnetic measurements, a new, analytically well-defined dark brown crystal modification (low-temperature form) of $OsCl_4$ is formed by heating, under reflux, a solution of OsO_4 in $SOCl_2$:

Although the strong chlorinating properties³¹ of $SOCl_2$ have been recognized, reaction (3), which leads to $OsCl_4$, has never previously been exploited.

b) Preparation of the high-temperature form of $OsCl_4$

500 mg. of OsO_4 was dissolved in 11 ml. of dry CCl_4 which was saturated at 300 °K with dry, oxygen-free chlorine gas immediately before use. This solution, sealed in a thick-walled glass tube of 30 cm. in length and 1 cm. in diameter, was heated in a 1 meter furnace to 743 °K for 24 hours. The initial reaction temperature of 743 °K was then lowered to 653 °K and was maintained there for further 48 hours. At the end of this period heating was stopped and the furnace was al-

²⁸ M. MERCER, Chem. Commun. [London] **1967**, 119.

²⁹ R. COLTON, Nature [London] **193**, 872 [1962].

³⁰ H. SCHÄFER, Chemische Transportreaktionen, page 13, Verlag Chemie, Weinheim 1962.

³¹ H. HECHT, G. JANDER, and H. SCHLAPMANN, Z. anorg. allg. Chem. **254**, 255 [1947].

lowed to cool down to 300 °K. A black sublimate was deposited at the cooler end of the sealed glass tube. The tube was opened and the sublimate was heated in vacuo at 323 °K for three hours to remove excess of CCl_4 .

c) *Preparation of the low-temperature form of OsCl_4*

500 mg. of OsO_4 , dissolved in 75 ml. freshly distilled SOCl_2 , was heated under reflux for 12 hours at 353 °K. Precautions were observed to prevent access of moist air, including the passage of dry nitrogen gas through the reaction vessel. Within 12 hours of reaction time under the experimental conditions specified, a dark brown precipitate was formed the purification of which was carried out in a glove box. Specifically, the excess of SOCl_2 was decanted from the precipitate. The residue was then washed several times with petroleum ether to remove excess of SOCl_2 . This sample was finally heated at 373 °K in vacuo for three hours before being analysed.

COLTON and FARTHING¹⁴ modified later this procedure¹ by leaving a solution of OsO_4 in SOCl_2 for one week at 300 °K.

d) *Elemental analysis*

In order to estimate both the osmium and the chlorine content of the reaction products isolated, the specimens were reduced to osmium metal in a current of dry hydrogen gas at 573 °K for 8 hours. The temperature was raised gradually from 300 °K to 573 °K in order to prevent loss of OsCl_4 by sublimation. Finally the temperature was raised to 773 °K for 2 hours to complete the reaction. The amount of hydrogen chloride evolved as a result of the quantitative reduction of OsCl_4 was absorbed in solutions of NaOH (2 N). To displace all the hydrogen chloride released, the system was flushed with nitrogen gas at 300 °K. The chlorine content was estimated gravimetrically by precipitation

as AgCl . The weight of the residue left over in the porcelain boat was used to estimate the content of osmium in OsCl_4 . The residue was identified by x-ray diffractometry to be pure osmium metal. An elemental analysis of the high-temperature form gave the following result:

	% Os	% Cl
Experimental:	57.5	42.6
Theoretical:	57.27	42.73

An elemental analysis of the low-temperature form yielded:

% Os	% Cl
57.4	42.8

e) *x-ray powder photographs*

These were obtained at 300 °K using nickel-filtered $\text{Cu-K}\alpha$ radiation and two Debye-Scherrer cameras of 5.73 and 11.48 cm. diameters. The samples were contained in 0.5 mm. Lindemann glass capillary tubes. The line intensities, I , were estimated visually on a 10 point scale.

f) *Magnetic measurements*

The magnetic susceptibilities were measured by the Gouy method with magnetic fields up to 10000 Oersteds. The samples were finely powdered and carefully packed in one half of the tube. The tube was evacuated and appropriate corrections were made for its diamagnetism. None of the compounds had a field dependent susceptibility beyond experimental error. The complex $\text{Hg}[\text{Co}(\text{SCN})_4]$ was used to calibrate³² the magnetic field.

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³² B. N. FIGGIS and R. S. NYHOLM, J. chem. Soc. [London] 1958, 4190.