using at first the heavy atom method. Afterwards the contributions of the light atoms were introduced in the calculated structure factors. Fig. 1 shows the electron density projection on (001).

Both structures are similar, therefore we have chosen the indium-C_5H_5 for successive refinement because the lighter metal-atom would give the possibility of reaching smaller standard errors in the position of the aromatic ring. Using the Cochran method of difference syntheses at the present stage we have obtained the following reliability factors:

$$hk0 \text{ reflexions: } R = 0{\cdot}08, \quad 0kl \text{ reflexions: } R = 0{\cdot}07$$

We have calculated that the actual co-ordinates are affected with the following standard errors:

$$\text{In: } \sigma_r = \pm 0{\cdot}01 \text{ Å and C: } \sigma_r = \pm 0{\cdot}07 \text{ Å}$$

The packing of the molecules in the crystal can be better explained with the aid of Fig. 2, where three chains of molecules are partially represented.

The structure is characterized by a chain disposition of the metal atoms and of the rings enclosed between them, at the same distance from both metals. The angular disposition of the system ring-metal-ring is characterized by an angle of 137° ± 30 min at the metal. The metal-ring distance is 3·19 ± 0·10 Å. The packing of the chains allows a minimal distance of 3·99 Å between metal-atoms belonging to adjacent chains. As can be seen, there is a zig-zag of equidistant metal-atoms, the angle M–M–M being about 100°.

The difference between the metal–ring distances in the gas phase[4] and in the solid-state is very large. This difference determines a great change of structure: in the gas phase there is the monomeric 'half sandwich' structure formed by one metal-atom and one aromatic ring; in the solid phase there is a polymeric structure formed by zig-zag chains. The chains are held together by a zig-zag of metal-atoms: the metal-metal distance is such as to allow the possibility of interaction between them.

It should be noted that every metal-atom is surrounded by two rings with the geometrical characteristics of the angular 'sandwich' structure.

The polymeric character explains the insolubility of the complex noted at first by E. O. Fischer.

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CHEMISTRY

Anhydrous Ruthenium Chlorides

THE contrasting magnetic behaviour (Table 1 and Fig. 1) of the α- and β-forms of $RuCl_3$ is of interest in relation to the different types of stereochemical arrangements[1] shown by the transition metal halides: it has also allowed the presence of α-$RuCl_3$, produced in the usual method of preparation of β-$RuCl_3$, to be detected. A material, hitherto considered[2,3] as yet another form of $RuCl_3$, is now shown to be $Ru_2^{IV}OCl_6$ (Table 1), a member of a class of oxide chlorides of binuclear ruthenium in which the average oxidation state of ruthenium changes from +4 through +3·5 to +3.

α-$RuCl_3$. This is produced[3,4] by a slow reaction between the metal and chlorine in siliceous vessels at temperatures above 600° C. However, contact of the metal with the silica causes the α-$RuCl_3$ to be contaminated with the soluble and relatively volatile oxide chloride, Ru_2OCl_6 (since this is diamagnetic its presence lowers the susceptibility observed and accounts for the values previously reported[5] being 16–19 per cent lower than ours). To avoid this contamination, α-$RuCl_3$ has now been prepared by heating β-$RuCl_3$ at or above the transition temperature for the β → α transformation. We have found, using the susceptibility as a means of analysis, that this transformation occurs slowly ($t_{\frac{1}{2}}$, about 1 h) at about 450° C, a temperature appreciably lower than the > 500° previously noticed[4]. The molar susceptibility, χ_M, of α-$RuCl_3$ between 77° and 300° K is shown in Fig. 1; at very low temperatures it decreases:

Temperature (° K)	77·3	20·4	4·2
$\chi_M \times 10^6$, E.M.U.	9,500	15,400	9,950 (all ± 200)

suggesting that α-$RuCl_3$ becomes antiferromagnetic. Neutron diffraction measurements (by G. E. Bacon) at 4·2° K confirm this behaviour and indicate a small magnetic moment (about 0·2 *B.M.*) on each ruthenium atom. The Néel temperature, T_N, about 30° K, is of the same order as those, 17° and 15° K respectively, reported[6] for $CrCl_3$ and $FeCl_3$.

Table 1

Compound	Appearance	Solubility	Magnetic behaviour	Structure
α-$RuCl_3$	Black, lustrous	Insoluble	With $A = 1{,}000$ cm^{-1}, μ_{eff} is 2·14 B.M. at 300° K, and θ is 32–40°. Antiferromagnetic, T_N, about 30° K	Hexagonal, layered (ref. 4); $a = 5{\cdot}99$, $c = 17{\cdot}22$ Å. Ru atoms have octahedral bonding with d_ε^5 configuration
β-$RuCl_3$ (metastable)	Dark-brown fluffy	Soluble in EtOH	χ_M low and decreases as temperature falls (Fig. 1)	Hexagonal, layered; $a = 6{\cdot}12$, $c = 5{\cdot}66$ Å. Ru atoms probably have tetrahedral bonding with $d_\gamma^4 d_\varepsilon^1$ configuration.
Ru_2OCl_6	Dark-brown hygroscopic	Soluble in H_2O and EtOH	Diamagnetic	Probably linear Ru—O—Ru, cf. $[Ru_2OCl_{10}]^{4-}$

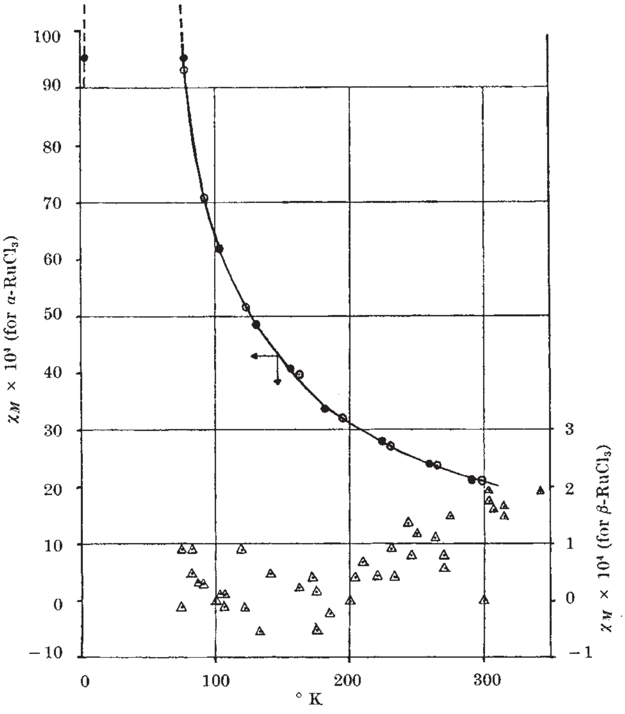

Fig. 1. Observed molar susceptibilities: ○, ●, Results for two separate preparations of α-$RuCl_3$; △, results from five separate sets of measurements between 77° and 345° K on the same preparation of β-$RuCl_3$, heated for 4 h at temperatures between 400° and 440° C between each successive set of measurements

β-RuCl$_3$. This is made[7] by heating ruthenium metal in a stream of carbon monoxide and chlorine. The susceptibilities of preparations made at 360°–390° C indicate the presence of 10–15 per cent of α-RuCl$_3$; this was not detected in the X-ray patterns until the materials had been annealed. β-RuCl$_3$ (found: Ru, 48·3; Cl, 50·5 per cent), almost free from α-RuCl$_3$ and certainly free from residual metal, has therefore been made at a temperature (340° C) lower than formerly used but sufficiently high for the carbonyl intermediate, probably Ru(CO)$_2$Cl$_2$, to be absent. The small increase in the observed susceptibility below 100° K (Fig. 1) is attributed to a trace (<2 per cent) of α-RuCl$_3$ in the sample.

Oxide Chlorides. Ru$_2$OCl$_6$ is one of several relatively volatile oxide chlorides which can be formed from the water-soluble mixture of aquochloro complexes[8] of polynuclear Ru(IV) known as "commercial ruthenium trichloride". This, when dried at 110°, consists largely of $(Ru_2O)^{6+}$ complexes, and after further heating at 300° in a stream of chlorine, leaves a dark-brown hygroscopic residue, mainly Ru$_2$OCl$_6$. Such a residue had a chlorine/ruthenium ratio of 3·04; the average oxidation state of ruthenium was $+3{\cdot}96$; and the absorption spectrum of a solution in 1 N acid, had λ_{max} 390 mμ, $\varepsilon_{Ru} = 5{,}600$, characteristic[8] of Ru_2O^{6+} complexes. It appeared amorphous to X-rays and was diamagnetic. When, however, the heating at 300° is carried out in a vacuum instead of a stream of chlorine, other oxide chlorides, Ru$_2$OCl$_5$ and Ru$_2$OCl$_4$, which have ruthenium respectively in the $+3{\cdot}5$ (ref. 9) and $+3$ oxidation states, are formed. A typical product had the ratio chlorine/ruthenium = 2·60, and an average oxidation state of $+$ 3·74: these, together with the spectrum of its solution, indicate a mixture of the following mole fractions: 0·62 Ru(IV) as $(Ru_2O)^{6+}$, 0·06 Ru(IV) as RuO$_2$, 0·22 Ru 3·5 as $(Ru_2O)^{5+}$, and 0·10 Ru(III) as $(Ru_2O)^{4+}$. The material was paramagnetic, χ_g being $0{\cdot}74 \times 10^{-6}$ E.M.U. at 299° K and rising to 1·57 at 90° K. The brown hygroscopic substance observed[2,3] to accompany α-RuCl$_3$ when prepared from the metal and chlorine at 600°–700° C was identified as Ru$_2$OCl$_6$ by the absorption spectrum of its aqueous solution and by the oxidation state of ruthenium.

Interpretation of Susceptibilities. The layered structure and cell dimensions[4] (Table 1) of α-RuCl$_3$ imply that each ruthenium atom occupies a position in which it is bonded octahedrally to six chlorine atoms. We assume: (1) that a strong ligand field exists for Ru^{3+} in the compound giving it a d_ε^5 configuration; (2) that there is a fairly strong spin-orbit interaction[10,11], such that the coupling constant, A (in ° K), is $>T$. It then follows[10] that $\mu^2{}_{eff} = 3 + 8T/A$ and that $\chi'_M = \dfrac{3 + 8T/A}{8(T - \theta)}$, where θ is a measure of the net magnetic interaction between the ruthenium ions. Although A for Ru^{3+} has been assessed[1] at 2,250° K, results[12] for Ru(III) complexes (for which θ should be nearly zero) give values in the range 1,000–2,000° K. Substituting $A = 1{,}500°$ K ($\equiv$ 1,000 cm^{-1}), and adjusting the values of χ_M to χ'_M by adding 100×10^{-6} E.M.U. for the diamagnetism of the ion cores, it is found that θ is 40° at 300° K and decreases to about 32° at 80° K (cf. θ = 31° for CrCl$_3$) (ref. 13). μ_{eff} is 2·14 Bohr magnetons at 300° K. The positive value of θ implies that the antiferromagnetic coupling between the ruthenium atoms in adjacent layers is weak compared with the ferromagnetic coupling between the ruthenium atoms within a layer.

The low values of χ_M shown by β-RuCl$_3$ are explained by each ruthenium atom occupying a position in a layered structure where it is bonded tetrahedrally to four chlorine atoms: this configuration may well be favoured by a 4-co-ordinated complex, Ru(CO)$_2$Cl$_2$, being an intermediate. On Kotani's[10] theory, Ru^{3+}, when tetrahedrally bonded and spin-paired, takes a $d_\gamma^4 d_\varepsilon^1$ configuration and, provided again that $A > T$, its magnetic moment is low, μ_{eff} being given by $\sqrt{4\ T/A}$ and χ'_M by $[2A(1-\theta/T)]^{-1}$: using again the value of 1,500° K for A, χ'_M would be $\sim 330 \times 10^{-6}$ E.M.U. at 300° K. In fact, χ'_M (that is, $\chi_M + 100 \times 10^{-6}$ E.M.U.) for β-RuCl$_3$ is found to be about 280×10^{-6} E.M.U. at 300° K. The fall in χ_M (Fig. 1) and hence in χ'_M as the temperature is lowered implies that θ in this case is negative, but a reasonable value for θ does not account for the observed fall.

It appears that β-RuCl$_3$ is metastable, the $\beta \rightarrow \alpha$ transformation being exothermic[4] and irreversible, and its density[4] being lower than that of α-RuCl$_3$.

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Electron Spin Resonance in Polymer Carbons: Effect of Halogens and Interhalogen Compounds

THE effect of adsorbed gases on the electron spin resonance signals of amorphous carbons has been reported by a number of workers[1–3]. In general, it has been found that whereas gases such as H$_2$, Ar, N$_2$ and Cl$_2$ (ref. 4) have no effect on the resonance signals, paramagnetic gases such as O$_2$ and NO have been found to have a large reversible effect at room temperature. This behaviour has been ascribed to the magnetic properties of the paramagnetic gas molecules.

Recent work in these laboratories has shown that the electron spin resonance signals of certain polymer chars are considerably modified by the adsorption of halogens and interhalogen compounds on to the carbon surface. Thus the adsorption of iodine from solution or from the vapour phase at room temperature by carbons prepared from polyvinylidene chloride (in the heat treatment range 300–1,000° C) caused a marked reduction in spin concentration at almost constant line width. The original signal was not restored by outgassing the carbon specimens at room temperature, but could be partially recovered by reheating the specimens in vacuum to 100° C.

The effect of Cl$_2$ and Br$_2$ was similar to that of I$_2$, leading to a partial or complete reduction in spin concentration depending on the carbon examined. In the reaction with chlorine at room temperature hydrochloric acid was detected in the gas phase using infra-red methods.

It should be noted that these effects are not observed with all amorphous carbons, a fact which may be explained on the basis of some of our earlier work[5], in which it was