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SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF THE MOLECULAR COMPLEX $[Ru(CO)_3Cl_2]_2 \cdot SbCl_3$

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Summary

The molecular complex $[Ru(CO)_3Cl_2]_2 \cdot SbCl_3$ has been prepared by reaction of antimony pentachloride and hydrogen chloride with ruthenium dodecacarbonyl in dichloromethane. Its molecular and crystal structure have been established by a single-crystal X-ray diffraction study. The structure consists of two crystallographically non-equivalent dimers $Ru_2(CO)_6Cl_4$ with a double Ru—Cl—Ru bridge, each dimer interacting with $SbCl_3$ units via Ru—Cl···Sb bonds. The coordination of the antimony trichloride fragment is discussed in terms of VSEPR (valence shell electron pair repulsion) on the assumption that the lone pair is playing a stereo-active role in the antimony environment. Crystallographic details: Space group: $P2_1/c$, $Z = 4$, $a = 9.289(2)$ Å, $b = 11.986(2)$ Å, $c = 16.932$ $c = 16.932(2)$ Å, $\beta = 100.31(2)°$. Final agreement factor for data with $I > 3\sigma(I)$: $R = 0.05$ for 1969 reflections.

Introduction

In the course of our investigation of the reaction between $SbCl_5$ and $Ru_3(CO)_{12}$, we have isolated the adduct $[Ru(CO)_3Cl_2]_2 \cdot SbCl_3$. Although a number of halogenocarbonyl ruthenium compounds are known [1—4], in only a few cases have they been structurally characterized by diffraction methods [5—7] and, in particular, data on chlorocarbonyl ruthenium complexes are lacking. Further interest in $[Ru(CO)_3Cl_2]_2 \cdot SbCl_3$ stems from the nature of the interactions between antimony trichloride and the dimeric species. It has been recognized for long that antimony trichloride can form molecular complexes known as electron-donor (or charge-transfer) complexes. Recently, adducts of this type have been characterized with halogenocarbonyl metal complexes [8—10].

Experimental

A suspension of 0.1 g of $Ru_3(CO)_{12}$ in 40 ml of CH_2Cl_2 was treated with $SbCl_5$ (0.05 ml) and gaseous HCl until dissolution was complete. The yellow solution was evaporated to a small volume and set aside overnight in a refrigerator, to give a yellow solid. This was filtered off and recrystallized twice (CH_2Cl_2) to yield pale yellow crystals of $[Ru(CO)_3Cl_2]_2 \cdot SbCl_3$. The compound is stable in dry air but rapidly destroyed by moisture.

A mass spectrum obtained from a Jeol Model J.M.S. D 100 mass spectrometer under operating conditions of 160 eV energy and a probe temperature of 40°C gives the major *m/e* peaks with correct isotopic abundance corresponding to $SbCl_3^+$, $SbCl_2^+$, $SbCl^+$, Sb^+, $Ru_2(CO)_6Cl_4^+$, $Ru_2(CO)_5Cl_4^+$, $Ru_2(CO)_4Cl_4^+$, $Ru_2(CO)_3Cl_4^+$, $Ru_2(CO)_2Cl_4^+$, $Ru_2(CO)Cl_4^+$, $Ru_2Cl_4^+$, $Ru_2Cl_3^+$, $Ru_2Cl_2^+$, $RuCl^+$ and Ru^+.

Crystal data

$[Ru(CO)_3Cl_2]_2 \cdot SbCl_3$; molecular weight: 740.39; monoclinic, $a = 9.289(2)$ Å, $b = 11.986(2)$ Å, $c = 16.932(2)$ Å, $\beta = 100.31(2)°$; $V = 1854.73$ Å^3; $D_0 = 2.60$ g cm^{-3}, $D_c = 2.65$ g cm^{-3}; $Z = 4$; Space group: $P2_1/c$.

Preliminary Weissemberg and precession photographs showed the crystal to belong to the monoclinic system $P2_1/c$. Lattice constants were determined by least-squares refinements of the angular positions of 25 reflections collected and centered on an Enraf-Nonius CAD 4 diffractometer. Diffraction data were collected at 295 K up to $2\theta = 60°$, using graphite monochromatized Mo-K_α radiation ($\lambda = 0.71069$ Å). The profile analysis of a few angle reflections indicated that an ω—$4/3\theta$ scan method was the most appropriate for data collection. Scan widths were calculated from the formula: $S_w = A + B \tan\theta$ where A depends on the mosaicity and was estimated from the profile analysis of a few low-angle reflections and B compensates for the increase in peak width due to K_{α_1}, K_{α_2} splitting. The values of A and B were 1.20 and 0.35, respectively. For each reflection, the calculated scan angle was extended by 25% on either side to estimate the background count. Three standard reflections were monitored every 60 reflections and showed no significant changes in intensity. Data were corrected for Lorentz and polarisation factors and absorption effects. The final data set consisted of 5570 independent reflections of which 1969 with $F_0^2 \geqslant 3\sigma(F_0^2)$ were used in the refinements.

Determination and refinement of the structure

The structure was solved in the space group $P2_1/c$ by direct methods, using the program MULTAN (11). All the atomic positional parameters and anisotropic temperature factors were refined by full-matrix least-squares procedure minimizing the function $\Sigma\omega(|F_0| - |F_c|)^2$ with $\omega^{-1} = \sigma^2_{\text{count}}(F_c)^2 + (0.01F_c)^2$, ($|F_0|$ and $|F_c|$ are the observed and calculated structure amplitudes). The value of the conventional agreement factor $R(F) = \Sigma|F_0| - |F_c|/\Sigma F_0$ was 0.057 and the value of the weighted factor $R_\omega(F) = (\Sigma\omega(|F_0| - |F_c|)^2/\Sigma|F_0|^2)^{1/2}$ was 0.048. The goodness-of-fit defined as $[\Sigma\omega(|F_0| - |F_c|)^2/(N - M)]^{1/2}$ where N is the number of observations (1969) and M the number of parameters varied (199), is 0.77. Final atomic coordinates are presented in Table 1. A table of anisotropic

TABLE 1

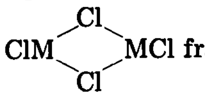
FINAL POSITIONAL PARAMETERS (10^{-4})

Atoms	x	y	z
Sb	6 369(1)	6 404(1)	1241(1)
Ru(A)	8 080(2)	10 362(1)	−272(1)
Ru(B)	8 687(2)	9 629(1)	4121(1)
Cl(1)	8 427(5)	6 734(5)	2246(3)
Cl(2)	4 839(5)	7 512(4)	1882(3)
Cl(3)	5 929(5)	4 711(3)	1849(3)
Cl(4A)	7 522(5)	9 040(4)	689(4)
Cl(5A)	10 221(5)	10 979(4)	687(2)
Cl(4B)	6 927(5)	10 599(4)	4738(3)
Cl(5B)	9 609(5)	8 850(3)	5432(2)
C(1A)	642(2)	982(1)	−96(1)
C(2A)	853(2)	1 135(2)	−107(1)
C(3A)	689(2)	1 142(2)	17(1)
C(1B)	800(2)	1 032(2)	307(1)
C(2B)	1 053(2)	884(1)	369(1)
C(3B)	734(2)	841(1)	391(1)
O(1A)	540(1)	952(1)	−140(1)
O(2A)	878(1)	1 189(1)	−158(1)
O(3A)	615(1)	1 201(1)	42(1)
O(1B)	764(1)	1 071(1)	250(1)
O(2B)	1 099(1)	835(1)	344(1)
O(3B)	654(1)	772(1)	382(1)

thermal parameters and a list of observed and calculated structure factors are available upon request from the authors.

Results and discussion

Significant interatomic distances and bond angles are listed in Tables 2 and 3 and Figs. 1 and 3. The crystal structure comprises two crystallographic non-equivalent, centrosymmetric dimeric molecules $[Ru(CO)_3Cl_2]_2$, which essentially differ in their respective interactions with the $SbCl_3$ units. The molecular structure of $[Ru(CO)_3Cl_2]_2$ can be described as a pair of octahedra sharing an edge formed by two bridging chlorine atoms. The two remaining chlorine atoms are *trans* to one bridging chlorine atom. As in isolated $[Ru(CO)_3Br_2]_2$ [5], the molecular point group symmetry is approximately $2/m$ (C_{2h}). In the $[Ru(CO)_3Cl_2]_2$ molecules, the independent C—O or Ru—C bond lengths do not differ significantly. The ruthenium atoms achieve the expected noble gas configuration without the need for metal—metal interactions. The geometry of the



$\mathrm{ClM}\overset{\mathrm{Cl}}{\underset{\mathrm{Cl}}{\quad}}\mathrm{MCl}$

fragment in each dimeric unit is very similar to that observed in the related complex $[\eta^5\text{-}C_5Me_5RhCl]_2(\mu\text{-}Cl)_2$ [12]. The ruthenium—terminal chlorine bond lengths are, as expected, slightly but significantly shorter than the ruthenium—bridging chlorine distances. The observed "non-bonding" Ru···Ru distances in the two crystallographically non-equivalent dimers are significantly different. In dimer A, in which the bridging chlorine atom Cl(5) does not interact with the $SbCl_3$ groups, the Ru—Cl(5) bridge is symmetric. In

TABLE 2

THE ENVIRONMENT OF THE ANTIMONY ATOMS

Symmetry operations implied by the subscript below:

a) x, 1.5 − y, −0.5 + z

b) 1 − x, −0.5 + y, 0.5 − z

c) 2 − x, 2 − y, −z

d) 2 − x, 2 − y, 1 − z

Atoms	Distances (Å)	Atoms	Angles (deg.)
Sb—Cl(1)	2.350(5)	Cl(1)—Sb—Cl(2)	92.9(2)
Sb—Cl(2)	2.351(5)	Cl(1)—Sb—Cl(3)	90.7(2)
Sb—Cl(3)	2.344(5)	Cl(1)—Sb—Cl(4A)	78.1(2)
Sb—Cl(4A)	3.516(5)	Cl(1)—Sb—Cl(4B)$_a$	70.0(2)
Sb—Cl(4B)$_a$	3.604(5)	Cl(1)—Sb—Cl(4B)$_b$	114.9(2)
Sb—Cl(4B)$_b$	3.347(5)	Cl(1)—Sb—Cl(5B)$_a$	70.0(2)
Sb—Cl(5B)$_a$	3.540(5)	Cl(2)—Sb—Cl(3)	96.8(2)
		Cl(2)—Sb—Cl(4A)	81.6(2)
		Cl(2)—Sb—Cl(4B)$_a$	151.6(2)
		Cl(2)—Sb—Cl(4B)$_b$	75.4(2)
		Cl(2)—Sb—Cl(5B)$_a$	148.8(2)
		Cl(3)—Sb—Cl(4A)	168.5(2)
		Cl(3)—Sb—Cl(4B)$_a$	78.0(2)
		Cl(3)—Sb—Cl(4B)$_b$	75.6(2)
		Cl(3)—Sb—Cl(5B)$_a$	108.9(2)
		Cl(4A)—Sb—Cl(4B)$_a$	108.7(2)
		Cl(4A)—Sb—Cl(4B)$_b$	115.0(2)
		Cl(4A)—Sb—Cl(5B)$_a$	69.7(2)
		Cl(4B)$_a$—Sb—Cl(4B)$_b$	72.2(2)
		Cl(4B)$_a$)—Sb—Cl(5B)$_a$	55.1(2)
		Cl(4B)$_b$—Sb—Cl(5B)$_a$	123.3(2)

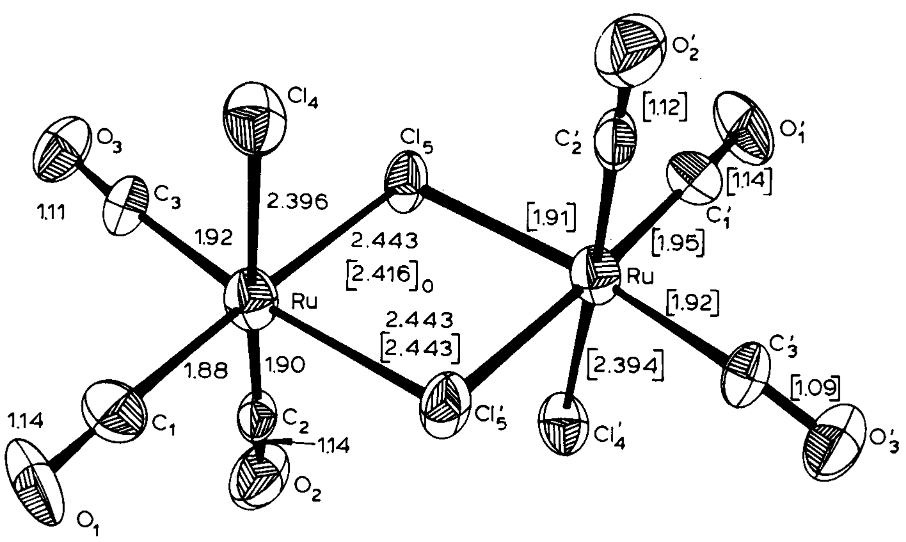


Fig. 1. Interatomic distances in the dimeric molecules of $[Ru(CO)_3Cl_2]_2$ (A and B). The superscript implies the symmetry operation through the inversion center which is designed by the hollow circle (values in parenthesis for dimer B).

TABLE 3

PRINCIPAL INTERATOMIC DISTANCES AND INTERBOND ANGLES IN THE DIMERIC MOLECULES OF $[Ru(CO)_3Cl_2]_2$ (A AND B)

Molecule A		Molecule B	
Atoms	Distances (Å)	Atoms	Distances (Å)
Ru(A)—Ru(A)$_c$	3.624(3)	Ru(B)—Ru(B)$_d$	3.600(3)
Ru(A)—Cl(4A)	2.396(4)	Ru(B)—Cl(4B)	2.394(5)
Ru(A)—Cl(5A)	2.443(4)	Ru(B)—Cl(5B)	2.416(4)
Ru(A)—Cl(5A)$_c$	2.443(4)	Ru(B)—Cl(5B)$_d$	2.443(4)
Ru(A)—C(1A)	1.88(2)	Ru(B)—C(1B)	1.95(2)
Ru(A)—C(2A)	1.90(2)	Ru(B)—C(2B)	1.91(2)
Ru(A)—C(3A)	1.92(2)	Ru(B)—C(3B)	1.92(2)
Ru(A)—O(1A)	3.02(1)	Ru(B)—O(1B)	3.04(1)
Ru(A)—O(2A)	3.04(1)	Ru(B)—O(2B)	3.02(1)
Ru(A)—O(3A)	3.04(1)	Ru(B)—O(3B)	3.01(1)
C(1A)—O(1A)	1.14(2)	C(1B)—O(1B)	1.14(2)
C(2A)—O(2A)	1.14(2)	C(2B)—O(2B)	1.12(2)
C(3A)—O(3A)	1.11(2)	C(3B)—O(3B)	1.09(2)
	Angles (deg.)		Angles (deg.)
C(1A)—Ru—C(2A)	91.5(7)	C(1B)—Ru—C(2B)	89.9(7)
C(1A)—Ru—C(3A)	90.7(7)	C(1B)—Ru—C(3B)	93.2(5)
C(1A)—Ru—Cl(4A)	87.1(5)	C(1B)—Ru—Cl(4B)	93.2(5)
C(1A)—Ru—Cl(5A)	177.0(5)	C(1B)—Ru—Cl(5B)	177.4(5)
C(2A)—Ru—C(3A)	95.0(7)	C(2B)—Ru—C(3B)	92.1(7)
C(2A)—Ru—Cl(4A)	177.1(5)	C(2B)—Ru—Cl(4B)	176.7(5)
C(2A)—Ru—Cl(5A)	91.5(5)	C(2B)—Ru—Cl(5B)	90.1(5)
C(3A)—Ru—Cl(4A)	87.6(5)	C(3B)—Ru—Cl(4B)	88.8(5)
C(3A)—Ru—Cl(5A)	89.7(5)	C(3B)—Ru—Cl(5B)	89.4(5)
Cl(4A)—Ru—Cl(5A)	89.9(2)	Cl(4B)—Ru—Cl(5B)	86.6(2)
Ru(A)—C(1A)—O(1A)	177(1)	Ru(B)—C(1B)—O(1B)	179(1)
Ru(A)—C(2A)—O(2A)	175(1)	Ru(B)—C(2B)—O(2B)	178(1)
Ru(A)—C(3A)—O(3A)	179(1)	Ru(B)—C(3B)—O(3B)	176(1)
Ru(A)—Cl(5A)—Ru(A)$_c$	97.7(1)	Ru(B)—Cl(5B)—Ru(B)$_d$	95.6(1)
Cl(5A)—Ru(A)—Cl(5A)$_c$	84.3(2)	Cl(5B)—Ru(B)—Cl(5B)$_d$	84.4(2)

contrast, in dimer B, the bridging chlorine atom has a short contact with antimony of 3.540(5) Å, which is less than the sum of the Van der Waals radii. This interaction with $SbCl_3$ results in a significant shortening of one of the Ru—Cl(5) bond, leading to an asymmetrical bridge and a shorter Ru···Ru distance.

The geometry of the $SbCl_3$ moiety in the complex is very similar to that of the corresponding fragment in pure crystalline $SbCl_3$ [13] with short Sb—Cl distances (mean values of 2.348(5) Å). However, the antimony atom completes its environment with a chlorines at longer distances ranging between 3.347(5) Å and 3.604(5) Å. The coordination around antimony cannot be satisfactorily described in terms of an idealized polyhedron geometry (Fig. 3). The valence-shell electron-pair repulsion concept predicts an arrangement invoking eight electron pairs including the lone pair (although the lack of any steric activity of the lone pair has already been observed in a neutral adducts of $SbCl_3$ [3]). In this case, the environment must be regarded as a much dis-

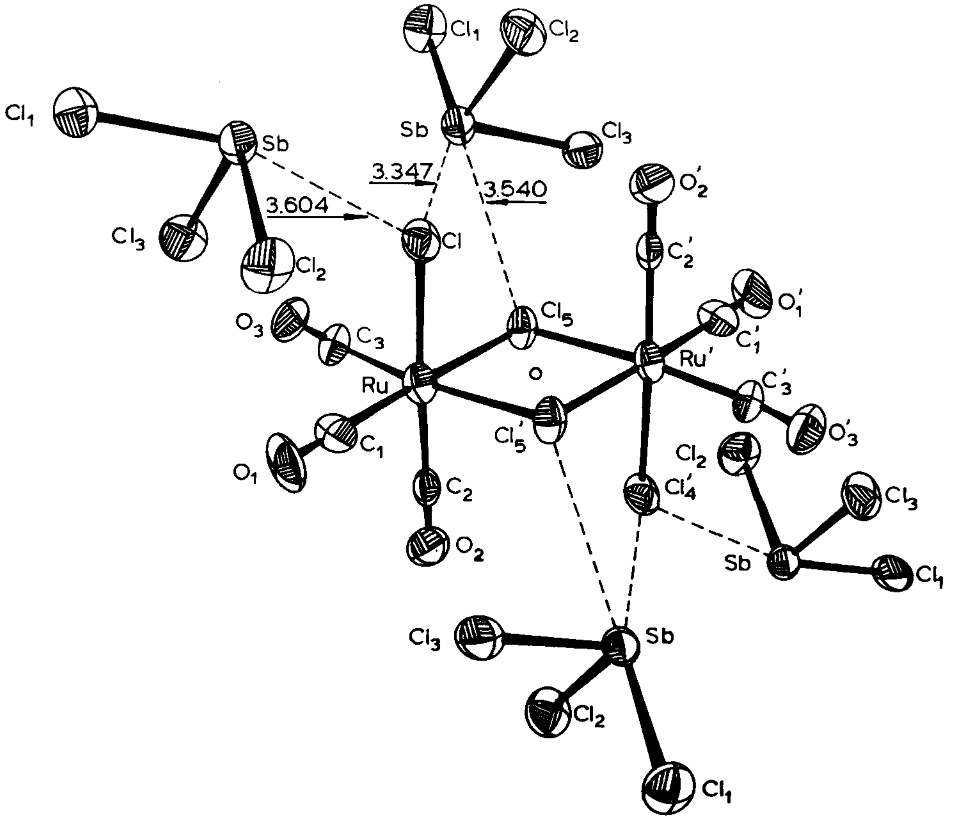


Fig. 2. Interactions between $SbCl_3$ and the dimeric molecule $[Ru(CO)_3Cl_2]_2$ (B).

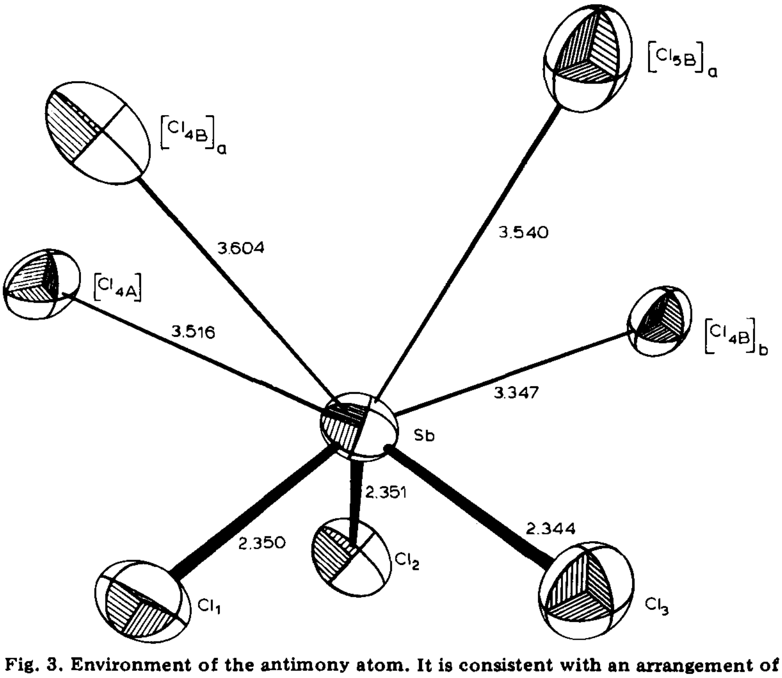


Fig. 3. Environment of the antimony atom. It is consistent with an arrangement of eight electronic pairs according to VSEPR theory. The subscripts a and b refer to the symmetry operations defined in Table 2.

torted 4,4-bicapped trigonal prism with a vacant site attributed to the unshared electron pair.

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