Formation and Structural Characterization of $[RuCl_2(CO)_2(SPh_2)_2]$, $[RuCl_2(CO)_3(OH_2)]$, and $[Ru(OH_2)_6][RuCl_3(CO)_3]_2 \cdot 2H_2O$

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While the room temperature reaction of $[RuCl_2(CO)_3]_2$ and Ph_2S in tetrahydrofuran in air affords $[RuCl_2(CO)_2(SPh_2)_2]$ (1) in moderate yield, that in dichloromethane results in the formation of a mixture of $[RuCl_2(CO)_3(H_2O)]$ (2) and $[Ru(H_2O)_6][RuCl_3(CO)_3]_2 \cdot 2H_2O$ (3). Very small amounts of 1 are produced only upon prolonged reflux of the reagents. All compounds were characterized by X-ray crystallography. 1 crystallizes as discrete octahedral *cis*(CO), *cis*(Cl), *trans*(Ph_2S) complexes, which are joined into stacks by weak $H \cdots Cl$ hydrogen bonds. 2 is also composed of discrete octahedral complexes. Four hydrogen bonds involving aqua and chlorido ligands link two complexes into a dimer. The structure of 3 consists of octahedral hexaaquaruthenium cations and two tricarbonyl-trichloridoruthenate anions. The water of crystallization is involved in hydrogen bonding between the cations and anions resulting in the formation of a continuous three-dimensional network.

Key words: Ruthenium Complex, Diphenyl Sulfide, Crystal Structure

Introduction

Mononuclear chalcogenoether complexes of ruthenium $[RuCl_2(CO)_2(ERR')_2]$ (E = S, Se, Te; R,R' = alkyl, phenyl) have been prepared by treatment of RR'E with RuCl₃ · nH₂O [1] or [RuX₂(CO)₃]_n (X = Cl, Br, I) [1-3]. The crystal structures, NMR spectroscopic information, and DFT calculations indicate that the cis(CO), cis(Cl), trans(ERR') isomer is energetically most favoured in each case [3]. The route for these complexes appears to involve the symmetric cleavage of bridging Ru-Cl bonds of the dinuclear ruthenium complex [2] with the formation of a [RuCl₂(CO)₃(ERR')] intermediate that has been isolated and structurally characterized in the case of Me₂Se [3]. The final substitution of CO that lies in the trans-position to the RR'E ligand by another molecule of the chalcogenide affords the end product $[RuCl_2(CO)_2(ERR')_2].$

The solvent seems to play a role in these substitution reactions. When the reaction was carried out in a coordinating solvent like tetrahydrofuran (THF), a mononuclear complex [RuCl₂(CO)₃(THF)] has been observed and identified by X-ray crystallography [3]. The crystal structure of this complex has recently been reported by Gray and Duffin [4]. It is probable that this species is an intermediate in the pathway to the monosubstituted $[RuCl_2(CO)_3(ERR')]$. We have, in fact, observed that the reaction of $[RuCl_2(CO)_3]_2$ and Ph₂S in THF produces $[RuCl_2(CO)_2(SPh_2)_2]$ (1) in moderate yield [3]. However, the analogous reaction of $[RuCl_2(CO)_3]_2$ and Ph₂Te in CH₂Cl₂ also affords $[RuCl_2(CO)_2(TePh_2)_2]$ in good yield [2].

In order to establish the significance of the solvent in these ligand substitution reactions we carried out the reaction of $[RuCl_2(CO)_3]_2$ and Ph_2S also in CH_2Cl_2 . Only very small amounts of **1** were obtained upon prolonged reflux of the reagents. At room temperature, a mixture of colourless crystals that turned out to be $[RuCl_2(CO)_3(OH_2)]$ (**2**) and $[Ru(H_2O)_6][RuCl_3(CO)_3]_2 \cdot 2H_2O$ (**3**) was formed. Since the reaction was carried out in air, the water originates from traces in the solvent or from humidity.

Experimental Section

SPh₂ (0.12 ml, 0.72 mmol, 0.134 g) was added to a suspension of [RuCl₂(CO)₃]₂ (0.081 g, 0.16 mmol) in CH₂Cl₂ (15 ml). The reaction mixture was stirred at room temperature for several days. *n*-Hexane was added to the filtered and concentrated solution and the mixture was cooled to -20 °C. The colourless crystals that were formed upon prolonged

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Compound	$C_{26}H_{20}Cl_2O_2RuS_2$ (1)	$C_3H_2Cl_2O_4Ru(2)$	$C_{3}H_{8}O_{7}Cl_{3}Ru_{1,5}$ (3)	Table 1. Details of the
Relative molecular mass	600.51	274.02	414.05	structure determination of
Crystal system	monoclinic	monoclinic	triclinic	$[\mathbf{D}_{\mathbf{r}}\mathbf{C}]$ (CO) (SDL) 1(1)
Space group	$P2_1P$	$P2_1/n$	ΡĪ	$[RuCl_2(CO)_2(SPIl_2)_2]$ (1),
a (Å)	6.475(1)	6.282(1)	6.246(1)	$[RuCl_2(CO)_3(OH_2)]$ (2),
$b(\mathbf{A})$	17.365(4)	10.332(2)	7.160(1)	and $[Ru(OH_2)_6][RuCl_3-$
<i>c</i> (Å)	11.629(2)	11.866(2)	14.800(3)	$(CO)_{2}_{2}_{2}_{2}_{2}_{2}_{2}_{2}_{2}_{2}$
α (deg)	90	90	91.80(3)	(00)312 21120 (0):
β (deg)	103.18(3)	97.73(3)	98.21(3)	
γ (deg)	90	90	115.16(3)	
$V(Å^3)$	1273.1(4)	763.1(3)	589.8(2)	
Ζ	2	4	2	
F(000)	604	520	398	
$D_c ({\rm g}{\rm cm}^{-3})$	1.567	2.385	2.332	
μ (Mo-K _{α}) (mm ⁻¹)	1.011	2.706	2.632	
<i>T</i> (K)	293(2)	150(2)	140(2)	
θ -Range for data collection	2.15 - 26.00	2.62 - 25.99	1.40 - 25.99	
Structure determination				
Crystal size (mm)	0.15 * 0.10 * 0.10	0.20 * 0.15 * 0.12	0.20 * 0.15 * 0.15	
Number of reflections collected	16141	5624	6119	
Number of unique reflections	4939	1456	2304	
Number of observed reflections ^a	4353	1347	2083	
Number of parameters/restrains	299/1	100/2	145/8	
RINT	0.0496	0.0182	0.0298	
$R_1^{\rm b}$	0.0334	0.0242	0.0564	
wR_2^{b}	0.0753	0.0571	0.1683	
R_1 (all data)	0.0447	0.0306	0.0618	
wR_2 (all data)	0.0880	0.0780	0.1731	
Goodness-of-fit	1.146	1.393	1.104	
Max and min heights in final	0.369-0.449	1.645 - 0.962	1.939-4.351	
difference Fourier synthesis ($e Å^{-3}$)				

^a $I \ge 2\sigma(I)$; ^b $R_1 = \sum ||F_0| - |F_c|| / \sum |F_0|, wR_2 = \{[\sum w(F_0^2 - F_c^2)^2] / [\sum w(F_0^2)^2]\}^{1/2}.$

standing were identified as a mixture of $[RuCl_2(CO)_3(H_2O)]$ (2) and $[Ru(H_2O)_6][RuCl_3(CO)_3]_2 \cdot 2H_2O$ (3).

The reaction was also carried out by refluxing 0.337 g (0.67 mmol) of $[RuCl_2(CO)_3]_2$ and 0.7 ml (4.20 mmol) of SPh₂ in 30 ml CH₂Cl₂ for 7 h. The solvent was evaporated from the filtrate. *n*-Hexane was added to the oily residue and the precipitate obtained was washed with hexane and dried. Elemental analysis and X-ray crystallographic measurements indicated that the precipitate was a mixture of $[RuCl_2(CO)_2(SPh_2)_2]$ (1) and $[RuCl_2(CO)_3]_2$.

Diffraction data of 1-3 were collected on a Nonius kappa CCD diffractometer using graphite monochromated Mo-K_{α} radiation ($\lambda = 0.71073$ Å). Crystal data and the details of the structure determination are shown in Table 1^{*}. The reflection data were corrected for Lorentz and polarization effects

and an empirical absorption correction was applied to the net intensities. The structures were solved by direct methods using SHELXS-97 [5] and refined using SHELXL-97 [6]. After the full-matrix least-squares refinement of the non-hydrogen atoms with anisotropic displacement parameters the hydrogen atoms were placed in calculated positions in the H₂O molecules (O-H = 0.82 Å) and the aromatic rings (C-H = 0.98 Å). The scattering factors for the neutral atoms were those incorporated with the programs.

Results and Discussion

The molecular structure of **1** is shown in Fig. 1 together with the atomic numbering scheme. Selected bond distances and angles are listed in Table 2. The structure consists of discrete complexes. The coordination polyhedron around ruthenium is a slightly distorted octahedron [the *cis* bond angles span a range of $83.86(5)-101.1(2)^{\circ}$]. The complex has the *cis*(CO), *cis*(C1), *trans*(SPh₂) ligand arrangement that was found to be the energetically most favoured isomer also by preliminary DFT calculations [3]. The two Ru-S bond lengths are 2.387(1) and

^{*}Crystallographic information (excluding tables of structure factors) for the compound **1** has been deposited with the Cambridgde Crystallographic Data Center as supplementary publication number CCDC 212907. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax. +44-1223-336-033; e-mail: deposit@ccde.cam.ac.uk). That for the compounds **2** and **3** has been deposited with the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany as supplementary publication no. CSD 413218 and 413219.

Table 2. Selected bond lengths (Å) and angles (°) in $[RuCl_2(CO)_2(SPh_2)_2]$ (1), $[RuCl_2(CO)_3(OH_2)]$ (2), and $[Ru(OH_2)_6][RuCl_3(CO)_3]_2 \cdot 2H_2O$ (3).

Bond length		Bond angle		
$[RuCl_2(CO)_2(SPh_2)]$	2](1)			
Ru(1)-S(1)	2.388(1)	S(1)-Ru(1)-C(2)	90.4(2)	
Ru(1)-S(2)	2.406(1)	S(2)-Ru(1)-Cl(1)	84.21(5)	
Ru(1)-Cl(1)	2.435(1)	S(2)-Ru(1)-Cl(2)	83.86(5)	
Ru(1)-Cl(2)	2.412(1)	S(2)-Ru(1)-C(1)	92.7(2)	
Ru(1)-C(1)	1.877(5)	S(2)-Ru(1)-C(2)	101.1(2)	
Ru(1)-C(2)	1.883(5)	Cl(1)-Ru(1)-Cl(2)	92.14(4)	
S(1)-C(111)	1.793(5)	Cl(1)-Ru(1)-C(1)	88.1(2)	
S(1)-C(121)	1.780(5)	Cl(1)-Ru(1)-C(2)	174.2(2)	
S(1)-C(211)	1.799(5)	Cl(2)-Ru(1)-C(1)	176.5(2)	
S(1)-C(221)	1.804(5)	Cl(2)-Ru(1)-C(2)	86.0(2)	
C(1)-O(1)	1.135(6)	C(1)-Ru(1)-C(2)	94.1(2)	
C(2)-O(2)	1.126(6)	C(111)-S(1)-C(121)	102.7(3)	
		C(211)-S(2)-C(221)	104.4(2)	
S(1)-Ru(1)-S(2)	166.19(4)	C(111)-S(1)-Ru(1)	112.7(2)	
S(1)-Ru(1)-Cl(1)	84.08(5)	C(121)-S(1)-Ru(1)	111.5(2)	
S(1)-Ru(1)-Cl(2)	89.28(5)	C(211)-S(2)-Ru(1)	114.5(2)	
S(1)-Ru(1)-C(1)	94.3(2)	C(221)-S(2)-Ru(1)	110.1(2)	
$[RuCl_2(CO)_3(OH_2)]$	(2)			
Ru(1)-C(1)	1.885(3)	C(2)-Ru(1)-0(4)	91.3(1)	
Ru(1)-C(2)	1.916(3)	C(3)-Ru(1)-0(4)	91.4(1)	
Ru(1)-C(3)	1.927(4)	C(1)- $Ru(1)$ - $Cl(1)$	89.14(9)	
Ru(1)-O(4)	2.148(2)	C(2)-Ru(1)-Cl(1)	179.26(8)	
Ru(1)-Cl(1)	2.408(1)	C(3)-Ru(1)-C1(1)	88.1(1)	
Ru(1)-Cl(2)	2.401(1)	O(4)-Ru(1)-Cl(1)	88.18(7)	
		C(1)-Ru(1)-Cl(1)	90.2(1)	
C(1)-Ru(1)-C(2)	91.4(1)	C(2)-Ru(1)-Cl(2)	88.59(9)	
C(1)-Ru(1)-C(3)	90.9(1)	C(3)-Ru(1)-Cl(2)	178.5(1)	
C(2)-Ru(1)-C(3)	92.5(1)	O(4)-Ru(1)-Cl(2)	87.49(7)	
C(1)-Ru(1)-O(4)	176.5(1)	Cl(1)-Ru(1)-Cl(2)	90.86(3)	
$[Ru(OH_2)_6][RuCl_3($	$(CO)_3]_2 \cdot 2H_2$	O (3)		
Ru(1)-O(11)	2.118(6)	C(21)-Ru(1)-C(23)	93.5(4)	
Ru(1)-O(12)	2.081(6)	C(21)-Ru(1)-Cl(21)	89.5(3)	
Ru(1)-O(.3)	2.070(6)	C(21)-Ru(1)-Cl(22)	178.5(3)	
Ru(2)-C(21)	1.899(10)	C(21)-Ru(1)-Cl(23)	89.1(3)	
Ru(2)-C(22)	1.879(9)	C(22)-Ru(1)-C(23)	91.7(4)	
Ru(2)-C(23)	1.911(10)	C(22)-Ru(1)-Cl(21)	174.9(3)	
Ru(2)-Cl(21)	2.426(2)	C(22)-Ru(1)-Cl(22)	88.5(3)	
Ru(2)-Cl(22)	2.422(2)	C(22)-Ru(1)-Cl(23)	86.6(3)	
Ru(2)-Cl(23)	2.410(2)	C(23)-Ru(1)-Cl(21)	92.5(3)	
	. /	C(23)-Ru(1)-Cl(22)	86.8(3)	
C(11)-Ru(1)-O(12)	92.3(3)	C(23)-Ru(1)-Cl(23)	176.9(3)	
C(11)-Ru(1)-O(13)	89.4(3)	Cl(21)-Ru(1)-Cl(22)	88.98(8)	
C(12)-Ru(1)-O(13)	89.2(3)	Cl(21)-Ru(1)-Cl(23)	89.10(8)	
C(21)-Ru(1)-C(22)	93.0(4)	Cl(22)-Ru(1)-Cl(23)	90.65(8)	

2.406(1) Å, similar to those in *mer*-[RuCl₃(SMe₂)₃] that range from 2.3843(8) to 2.4043(8) Å [7]. The respective Ru-Cl lengths of 2.412(1) and 2.435(1) Å are comparable to the Ru–Cl lengths of 2.436(2) and 2.444(2) Å in [RuCl₂(CO)₂(TePh₂)₂] [2] and expectedly slightly longer than those of 2.3388(8)–2.3497(8) Å in [RuCl₃(SMe₂)₃] that contains the



Fig. 1. The molecular structure of $[RuCl_2(CO)_2(SPh_2)_2]$ (1) indicating the numbering of the atoms. The thermal ellipsoids have been drawn at 50% probability.



Fig. 2. The weak hydrogen bonding network in $[RuCb-(CO)_2(SPh_2)_2]$ (1).



Fig. 3. The molecular structure of $[RuCl_2(CO)_3(OH_2)]$ (2) indicating the numbering of the atoms. The thermal ellipsoids have been drawn at 50% probability.



Fig. 4. Four hydrogen bonds in $[RuCl_2(CO)_3(OH_2)]$ (2) connect the complexes into dimeric units.

ruthenium atom in a higher positive oxidation state [7]. The Ru-C bond lengths of 1.877(5) and 1.883(5) Å in **1** are also comparable to those of 1.871(7) and 1.849(8) Å in [RuCl₂(CO)₂(TePh₂)₂] [2].

The $[RuCl_2(CO)_2(SPh_2)_2]$ complexes are packed into stacks by a weak three-dimensional $H\cdots Cl$ hy-



Fig. 5. The molecular structure of $[Ru(OH_2)_6][RuCl_3-(CO)_3]_2 \cdot 2H_2O$ (3) indicating the numbering of the atoms. The thermal ellipsoids have been drawn at 50% probability.



Fig. 6. The hydrogen bonding network in $[Ru(OH_2)_6]$ $[RuCl_3(CO)_3]_2 \cdot 2H_2O$ (3).

drogen bonding network that also binds the adjacent stacks together (see Fig. 2). The shortest intermolecular distances are 2.864-2.994 Å.

As shown in Fig. 3, the structure of $[RuCl_2(CO)_3-(OH_2)]$ (2) also consists of discrete complexes with the ruthenium atom showing slightly distorted octahedral coordination [the range of the *cis*-bond angles is $87.49(7)-92.47(13)^\circ$]. The three carbonyl groups are arranged facially, the octahedron being completed by two *cis*-chlorido and one aqua ligand. The Ru-Cl distances are 2.401(1) and 2.408(1) Å, the Ru-C bond

lengths span a range of 1.885(3)-1.927(4) Å, and the Ru-O bond length is 2.148(2) Å. In addition to the corresponding bond lengths in **1**, these values can be compared to those observed for [RuCl₂(CO)₃(OH₂)] in a diglyme adduct [8], which shows Ru-OH₂, Ru-C, and Ru-Cl bond lengths of 2.105(4), 1.889(5)-1.905(5) Å, and 2.395(3) Å, respectively. Both in **2** and in the diglyme complex the Ru-C bonds *trans* to the aqua ligand is shorter than the Ru-C bonds *trans* to the chlorido ligands.

The complexes of **2** are packed together in pairs by four $H \cdots Cl$ hydrogen bonds (see Fig. 4) that span a range of 2.326–2.399 Å. In the case of the diglyme adduct, diglyme acts as a hydrogen-bond acceptor for the coordinated water molecule [8]. The distance between the oxygen atoms of water molecules and the oxygen atoms of the diglyme molecules is 2.71 Å.

The molecular structure of 3 is shown in Fig. 5 together with the atomic numbering scheme, and the selected bond distances and angles are listed in Table 2. **3** is composed of $[Ru(OH_2)_6]^{2+}$ cations and $[RuCl_3(CO)_3]^-$ anions. Ruthenium shows octahedral coordination in both ions. The Ru-O bonds in the cation show lengths of 2.070(6) - 2.118(6) Å and can be compared to the Ru-O bonds in hexaaquaruthenium(II) p-toluenesulfonate that exhibit an average length of 2.122 Å [9]. The carbonyl and chlorido ligands in the $[RuCl_3(CO)_3]^-$ anion are in the facial configuration. The Ru-Cl distances range from 2.410(2) to 2.426(2) Å. They are near to the Ru-Cl bond lengths in 1 and 2 and are also comparable to the corresponding bonds in (H₅O₂)[RuCl₃(CO)₃]·SbCl₃ (average 2.419 Å) [10], $(S_5N_5)[RuCl_3(CO)_3]$ (average 2.412 Å) [11], and $[Ru(CO)_3(\eta - C_5H_5)][RuCl_3(CO)_3]$ (average 2.404 Å) [12]. The Ru-C bond lengths also show typical values ranging 1.879(9) - 1.914(9) Å (c.f. the corresponding bond lengths in 1 and 2).

The cations and anions of **3** are connected into a three-dimensional network by hydrogen bonding, as shown in Fig. 6. The water of crystallization is involved in four hydrogen bonds. There are two short oxygen-hydrogen distances of 1.880 and 1.957 Å $[H(11B)\cdots O(1) \text{ and } H(13B)\cdots O(1), \text{ respectively; the respective O-H···O angles are 176.4 and 161.8°] and two hydrogen-chlorine contacts of 2.350 and 2.578 Å <math>[H(1A)\cdots Cl(22) \text{ and } H(1B)\cdots Cl(21), \text{ respectively; the respective O-H···Cl angles are 175.9 and 145.6°]. The coordinated water molecules of the cation also form weak hydrogen bonds with the chlorido ligands of the anion.$

The reaction of $[RuCl_2(CO)_3]_2$ and SPh_2 in THF affords $[RuCl_2(CO)_2(SPh_2)_2]$ (1) in moderate yield [3]. The stirring of $[RuCl_2(CO)_3]_2$ and SPh_2 in CH_2Cl_2 at room temperature produces a mixture of $[RuCl_2(CO)_3(OH_2)]$ (2) and $[Ru(H_2O)_6][RuCl_3(CO)_3]_2 \cdot 2H_2O$ (3). A small amount of $[RuCl_2(CO)_2(SPh_2)_2]$ is obtained upon prolonged reflux of the reagents.

The formation of **2** and **3** in CH_2Cl_2 in air may be formulated as follows:

$$2[\operatorname{RuCl}_2(\operatorname{CO})_3]_2 \xrightarrow{\operatorname{H}_2\operatorname{O}} [\operatorname{RuCl}_2(\operatorname{CO})_3(\operatorname{OH}_2)] \\ + [\operatorname{Ru}(\operatorname{OH}_2)_6][\operatorname{RuCl}_3(\operatorname{CO})_3]_2 + 3\operatorname{CO}$$

Upon reflux, the aqua ligand in **2** is substituted by SPh_2 . [RuCl₂(CO)₂(SPh₂)₂] (**1**) is obtained by the subsequent substitution of CO by a second SPh_2 molecule. The very small yield may be explained by the formation of [Ru(OH₂)₆][RuCl₃(CO)₃]₂ that removes ruthenium from further reaction.

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