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Solid State Structure of Ru(η^5-C_5Me_5)(η^4-C_5H_4O)Br $\cdot$ 2[Et_3NH] $\cdot$ [Zn(Br,Cl)$_4$] – An Unusual Adduct

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Summary. Ru(η^5-C_5Me_5)(η^4-C_5H_4O)Br $\cdot$ 2[Et_3NH] $\cdot$ [Zn(Br,Cl)$_4$] was unexpectedly obtained during attempts to prepare the parent complex Ru(η^5-C_5Me_5)(η^4-C_5H_4O)Br in a one-pot synthesis. The crystal structure was determined by X-ray diffraction: monoclinic, space group $P2_1/a$, $a = 14.307(2)$ Å, $b = 12.819(2)$ Å, $c = 19.897(4)$ Å, $\beta = 95.98(1)°$, $V = 3629.3(11)$ Å^3, $Z = 4$, $R = 0.044$ for 3633 data ($I > 2\sigma(I)$). The compound represents the third crystalline form of Ru(η^5-C_5Me_5)(η^4-C_5H_4O)Br known so far. It is built from alternating layers of neutral Ru complexes, triethylammonium cations, and tetrahedral [Zn(Br,Cl)$_4$]$^{2-}$ anions. Remarkably, one of the two independent triethylammonium ions is hydrogen bonded to the cyclopentadienone oxygen of the neutral Ru complex.

Keywords. Ruthenium; Cyclopentadienone complexes; Pentamethylcyclopentadienyl complexes; X-ray structure.

Festkörperstruktur von Ru(η^5-C_5Me_5)(η^4-C_5H_4O)Br $\cdot$ 2[Et_3NH] $\cdot$ [Zn(Br,Cl)$_4$] – ein ungewöhnliches Addukt

Zusammenfassung. Ru(η^5-C_5Me_5)(η^4-C_5H_4O)Br $\cdot$ 2[Et_3NH] $\cdot$ [Zn(Br,Cl)$_4$] wurde überraschend bei Versuchen erhalten, den Mutterkomplex Ru(η^5-C_5Me_5)(η^4-C_5H_4O)Br in einer Eintopfsynthese herzustellen. Die Kristallstruktur wurde mittels Röntgenbeugung bestimmt: monoklin, Raumgruppe $P2_1/a$, $a = 14.307(2)$ Å, $b = 12.819(2)$ Å, $c = 19.897(4)$ Å, $\beta = 95.98(1)°$, $V = 3629.3(11)$ Å^3, $Z = 4$, $R = 0.044$ für 3633 Reflexe mit $I > 2\sigma(I)$. Die Verbindung ist die dritte bisher bekannte kristalline Form von Ru(η^5-C_5Me_5)(η^4-C_5H_4O)Br. Sie ist aus alternierenden Schichten von neutralen Ru-Komplexen, Triethylammoniumkationen und tetraedrischen [Zn(Br,Cl)$_4$]$^{2-}$-Anionen aufgebaut. Bemerkenswert ist, daß eines der beiden symmetrieunabhängigen Triethylammoniumionen über eine H-Brücke mit dem Cyclopentadienon-Sauerstoff des neutralen Ru-Komplexes verknüpft ist.

Introduction

We have previously reported on the synthesis and reactivity of complexes featuring the [Ru(η^5-C_5Me_5)(η^4-C_5H_4O)]$^+$ fragment [1]. Complexes of that type have been

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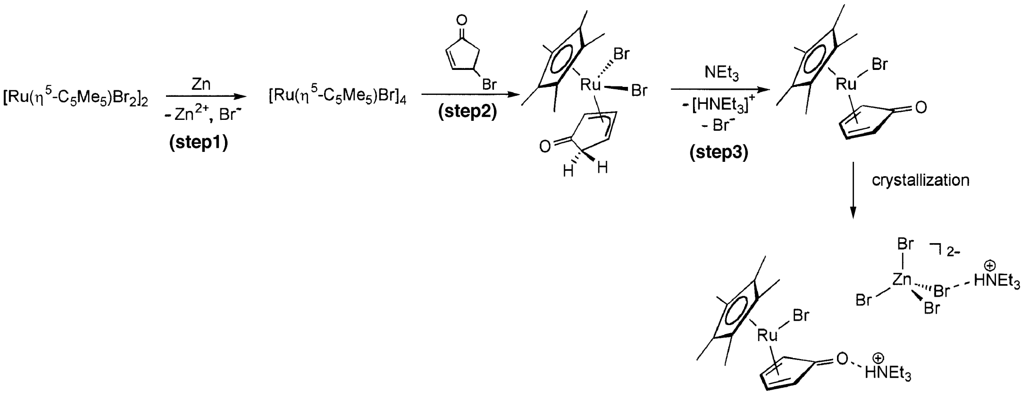
shown to undergo a variety of reactions, including nucleophilic additions on the α-carbon atom of the C_5H_4O ligand to give 1,2-disubstituted ruthenocenes [1] and electrophilic addition of water at the basic ketonic oxygen to afford the novel *bis*-water adduct $Ru(\eta^5\text{-}C_5Me_5)(\eta^4\text{-}C_5H_4O)Br \cdot 2H_2O$ [2]. Since the synthesis of the above complexes requires a multi-step procedure, we sought a more convenient route to the principle precursor complex $Ru(\eta^5\text{-}C_5Me_5)(\eta^4\text{-}C_5H_4O)Br$ *via* a one-pot synthesis starting from the readily available dimer $[Ru(\eta^5\text{-}C_5Me_5)Br_2]_2$. However, instead of obtaining the parent complex $Ru(\eta^5\text{-}C_5Me_5)(\eta^4\text{-}C_5H_4O)Br$, the rather unexpected adduct $Ru(\eta^5\text{-}C_5Me_5)(\eta^4\text{-}C_5H_4O)Br \cdot 2[Et_3NH] \cdot [Zn(Br,Cl)_4]$ was isolated. The structure of this compound is reported here.

Results and Discussion

The reaction pathway leading to the formation of the title compound is depicted in Scheme 1. Further informations on synthesis and crystal structure determination are given in the experimental section and in Tables 1 and 2. The title compound represents an unusual combination of a neutral sandwich complex $Ru(\eta^5\text{-}C_5Me_5)(\eta^4\text{-}C_5H_4O)Br$, two triethylammonium cations $[Et_3NH]^+$, and a tetrahedral $[Zn(Br,Cl)_4]^{2-}$ anion (Fig. 1). Besides *van der Waals* and electrostatic forces, the constituents are held together by hydrogen bonds. A view of the $Ru(\eta^5\text{-}C_5Me_5)(\eta^4\text{-}C_5H_4O)Br$ complex and the hydrogen bonded $[Et_3N(1)H]^+$ cation is shown in Fig. 2. The Ru complex is identical in stereochemistry and similar in bond lengths, bond angles, and conformation to the corresponding complexes $Ru(\eta^5\text{-}C_5Me_5)(\eta^4\text{-}C_5H_4O)Br$ [1] and its dihydrate $Ru(\eta^5\text{-}C_5Me_5)(\eta^4\text{-}C_5H_4O)Br \cdot 2H_2O$ [2]. The cyclopentadienone moiety is *exo*-oriented (oxygen pointing to the Br side of the complex) and shows an envelope conformation with a tilt angle of 18.0(4)° between its butadiene part (C(12) through C(15)) and its ketone part (O, C(11), C(12), C(15)). The angle between the butadiene part and the cyclopentadienyl ring of C_5Me_5 measures 36.7(2)°. Some geometric data of the Ru complexes in the three compounds are compared in Table 3. A lengthening of the C(11)–O bond can be noted for the title compound and the dihydrate, in both of which the keto oxygen



Scheme 1

Table 1. Atomic coordinates and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for non-hydrogen atoms of Ru(η^5-C_5Me_5)(η^4-C_5H_4O)Br · 2[Et_3NH] · [Zn(Br,Cl)$_4$]; U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor

	x	y	z	U_{eq}
Ru Complex				
Ru	0.28682(3)	0.15010(4)	0.38921(3)	40(1)
Br(1)	0.29014(6)	−0.04214(6)	0.35864(5)	76(1)
C(1)	0.1942(4)	0.2825(5)	0.4079(4)	49(2)
C(2)	0.1694(4)	0.2477(5)	0.3397(3)	47(2)
C(3)	0.1377(4)	0.1446(5)	0.3426(4)	50(2)
C(4)	0.1405(4)	0.1161(5)	0.4135(4)	56(2)
C(5)	0.1754(5)	0.2008(6)	0.4536(4)	56(2)
C(6)	0.2210(5)	0.3917(5)	0.4284(4)	67(2)
C(7)	0.1701(5)	0.3105(6)	0.2766(4)	67(2)
C(8)	0.0975(5)	0.0790(6)	0.2847(4)	76(3)
C(9)	0.0985(5)	0.0175(6)	0.4384(5)	82(3)
C(10)	0.1852(6)	0.2094(7)	0.5294(4)	90(3)
C(11)	0.4599(4)	0.0941(5)	0.3855(4)	51(2)
C(12)	0.4183(4)	0.1723(5)	0.3377(4)	53(2)
C(13)	0.3957(4)	0.2601(5)	0.3739(4)	55(2)
C(14)	0.4012(4)	0.2322(5)	0.4431(4)	58(2)
C(15)	0.4284(5)	0.1277(5)	0.4495(4)	53(2)
0	0.5062(3)	0.0159(4)	0.3743(3)	63(1)
Triethylammonium cation 1				
N(1)	0.5113(4)	−0.1334(4)	0.2728(3)	54(2)
C(16)	0.4779(5)	−0.2302(6)	0.3030(4)	71(2)
C(17)	0.5256(7)	−0.2524(7)	0.3708(4)	91(3)
C(18)	0.4514(8)	−0.1129(7)	0.2071(5)	104(3)
C(19)	0.4491(10)	−0.0141(10)	0.1813(6)	163(6)
C(20)	0.6141(5)	−0.1315(6)	0.2684(4)	74(2)
C(21)	0.6512(6)	−0.2244(7)	0.2320(5)	100(3)
Triethylammonium cation 2				
N(2A)[a]	0.3664(11)	0.6995(12)	−0.0071(8)	77(4)
N(2B)[a]	0.3404(15)	0.7693(16)	−0.0349(11)	111(6)
C(22)	0.2717(10)	0.7454(12)	0.0036(8)	159(6)
C(23)	0.2444(14)	0.8111(12)	0.0501(8)	218(9)
C(24)	0.3674(17)	0.6405(29)	−0.0627(14)	377(24)
C(25)	0.3141(13)	0.5879(14)	−0.0962(13)	260(13)
C(26)	0.4280(13)	0.7835(22)	−0.0172(16)	382(25)
C(27)	0.4965(11)	0.8306(14)	−0.0096(10)	216(9)
[Zn(Br,Cl)$_4$]$^{2-}$ anion				
Zn	0.35590(6)	0.48213(6)	0.17516(4)	54(1)
Br(2)[b]	0.39327(7)	0.30117(7)	0.16469(5)	65(1)
Br(3)[b]	0.35166(7)	0.53197(7)	0.29055(5)	64(1)
Br(4)[b]	0.47095(8)	0.58899(9)	0.12933(6)	81(1)
Br(5)[b]	0.20728(7)	0.51018(10)	0.11112(6)	89(1)

[a] Second triethylammonium moiety disordered with nitrogen in two half-occupied positions; [b] Br sites with mixed occupation by Br and Cl, refined site occupancy factors of 0.698(3) for Br and 0.302(3) for Cl

Table 2. Selected bond lengths (Å) and angles (°) for $Ru(\eta^5\text{-}C_5Me_5)(\eta^4\text{-}C_5H_4O)Br \cdot 2[Et_3NH] \cdot [Zn(Br,Cl)_4]$

Distances		Zn–Br(4)	2.394(1)
		Zn–Br(5)	2.390(1)
Ru–C(1)	2.209(6)		
Ru–C(2)	2.238(6)	Hydrogen bonds	
Ru–C(3)	2.237(6)		
Ru–C(4)	2.239(6)	N(1)...O	2.790(7)
Ru–C(5)	2.244(7)	N(2A)...Br(4)	3.28(2)
Ru–C(11)	2.587(6)	N(2B)...Br(5)	3.48(2)
Ru–C(12)	2.252(6)		
Ru–C(13)	2.147(6)	Angles	
Ru–C(14)	2.137(6)		
Ru–C(15)	2.262(6)	C(2)–C(1)–C(5)	109.2(6)
Ru–Br(1)	2.540(1)	C(2)–C(1)–C(6)	125.4(6)
		C(5)–C(1)–C(6)	124.8(7)
C(1)–C(2)	1.437(9)	C(1)–C(2)–C(3)	107.7(6)
C(1)–C(5)	1.431(9)	C(1)–C(2)–C(7)	127.2(6)
C(1)–C(6)	1.497(9)	C(3)–C(2)–C(7)	125.0(7)
C(2)–C(3)	1.401(9)	C(2)–C(3)–C(4)	107.5(6)
C(2)–C(7)	1.494(9)	C(2)–C(3)–C(8)	126.9(7)
C(3)–C(4)	1.452(10)	C(4)–C(3)–C(8)	125.3(6)
C(3)–C(8)	1.493(9)	C(3)–C(4)–C(5)	109.3(6)
C(4)–C(5)	1.408(10)	C(3)–C(4)–C(9)	123.9(7)
C(4)–C(9)	1.506(9)	C(5)–C(4)–C(9)	126.2(7)
C(5)–C(10)	1.503(10)	C(1)–C(5)–C(4)	106.4(6)
		C(1)–C(5)–C(10)	125.4(7)
C(11)–O	1.234(8)	C(4)–C(5)–C(10)	128.1(7)
C(11)–C(12)	1.464(9)		
C(11)–C(15)	1.460(9)	C(12)–C(11)–O	129.0(7)
C(12)–C(13)	1.394(9)	C(15)–C(11)–O	128.0(7)
C(13)–C(14)	1.416(10)	C(12)–C(11)–C(15)	102.9(6)
C(14)–C(15)	1.397(9)	C(11)–C(12)–C(13)	108.5(7)
		C(12)–C(13)–C(14)	107.8(6)
N(1)–C(16)	1.479(9)	C(13)–C(14)–C(15)	108.5(7)
N(1)–C(18)	1.510(10)	C(11)–C(15)–C(14)	108.1(7)
N(1)–C(20)	1.483(9)		
C(16)–C(17)	1.475(11)	Br(2)–Zn–Br(3)	111.8(1)
C(18)–C(19)	1.366(13)	Br(2)–Zn–Br(4)	110.7(1)
C(20)–C(21)	1.517(10)	Br(2)–Zn–Br(5)	107.1(1)
		Br(3)–Zn–Br(4)	107.5(1)
Zn–Br(2)	2.394(1)	Br(3)–Zn–Br(5)	111.2(1)
Zn–Br(3)	2.390(1)	Br(4)–Zn–Br(5)	108.7(1)

is a hydrogen bond acceptor, whereas in $Ru(\eta^5\text{-}C_5Me_5)(\eta^4\text{-}C_5H_4O)Br$ it is not. In title compound, the keto oxygen accepts one relatively short and straight hydrogen bond from the $[Et_3N(1)H]^+$ cation ($N(1)\cdots O = 2.790(7)$ Å, Fig. 2); in the dihydrate [2], it accepts two hydrogen bonds from the water molecules

Table 3. Comparison of selected geometric data of the [Ru(η^5-C_5Me_5)(η^4-C_5H_4O)Br] complex in the title compound (**1**), in Ru(η^5-C_5Me_5)(η^4-C_5H_4O)Br (**2**), and in Ru(η^5-C_5Me_5)(η^4-C_5H_4O)Br · $2H_2O$ (**3**) (*cp* = cyclopentadienyl, *cpd* = C_5H_4O = cyclopentadienone; the last three lines give the angles between the least-squares planes of butadiene (C(12), C(13), C(14), C(15)), ketone (O, C(11), C(12), C(15)), and *cp*-ring (C(1), C(2), C(3), C(4), C(5))

	1	**2**	**3**
$\langle Ru-C_{cp} \rangle$	2.233(6)	2.232(3)	2.221(8)
$\langle Ru-C_{cpd} \rangle$	2.200(6)	2.187(3)	2.187(7)
Ru–Br	2.540(1)	2.547(1)	2.535(1)
Ru–C(11) (non-bonding)	2.587(6)	2.625(4)	2.587(8)
$\langle C_{cp}-C_{cp} \rangle$ ring	1.426(9)	1.428(3)	1.425(11)
$\langle C_{cp}-C_{Me} \rangle$ terminal	1.499(10)	1.501(3)	1.499(11)
⟨C(11)–C(12), C(11)–C(15)⟩	1.462(9)	1.470(4)	1.458(10)
⟨C(12)–C(13), C(14)–C(15)⟩	1.400(9)	1.392(4)	1.384(11)
C(13)–C(14)	1.416(10)	1.400(5)	1.420(11)
C(11)–O	1.234(8)	1.216(5)	1.240(8)
butadiene ∠ ketone	18.0(4)	24.9(2)	20.2(4)
cp-ring ∠ butadiene	36.7(2)	35.8(2)	37.7(5)
cp-ring ∠ ketone	54.6(2)	60.7(1)	57.9(4)

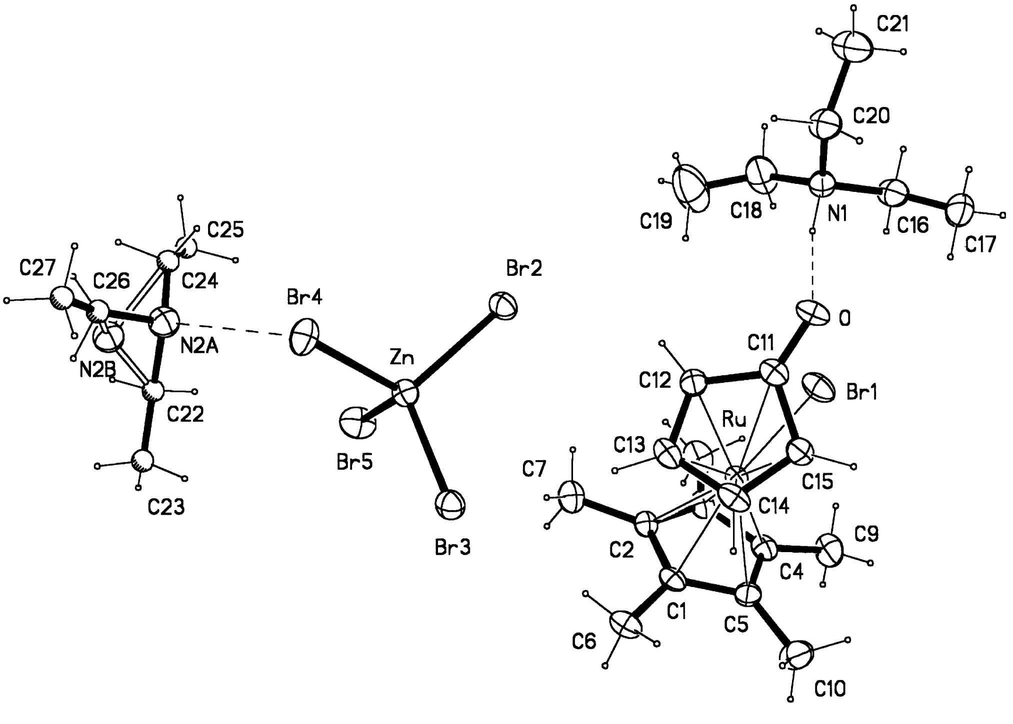


Fig. 1. Asymmetric unit of Ru(η^5-C_5Me_5)(η^4-C_5H_4O)Br · 2[Et_3NH] · [Zn(Br,Cl)$_4$]; N(2a) and N(2b) are two alternatively occupied sites

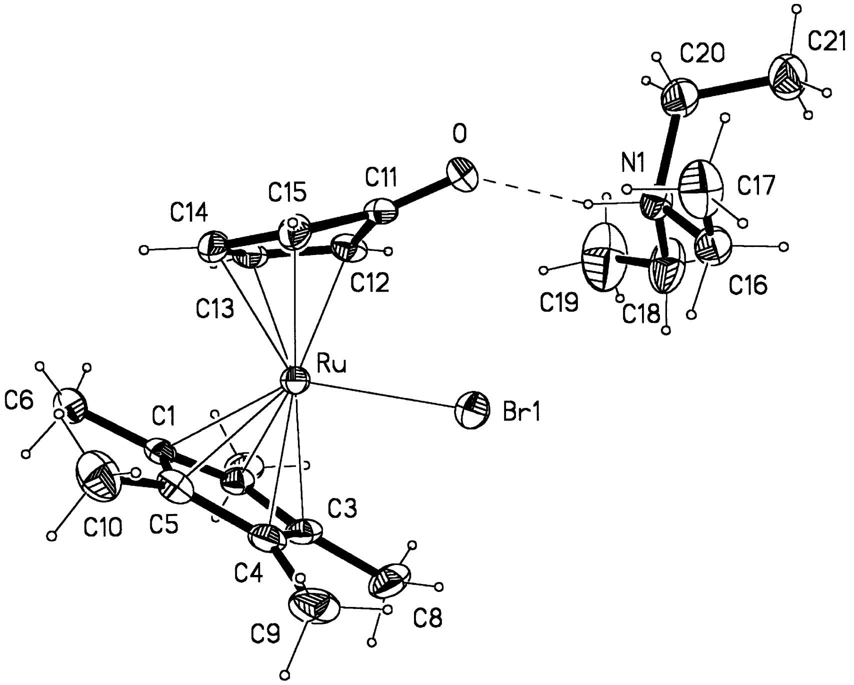


Fig. 2. Ru complex and the hydrogen bonded [$Et_3N(1)H$] (20% ellipsoids)

(O···O = 2.89 and 2.82 Å). This hydrogen bond acceptor capability of the cyclopentadienone oxygen is considered not only as result of the polarization of the cyclopentadienone moiety, but should be supported by the distinct electron donating property of the C_5Me_5 ligand. Interestingly, a hydrogen bond acceptor function has recently been observed for the cyclopentadienone oxygen in the cationic Ru complex $[Ru(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_5H_4O)(SC(NH_2)_2)]CF_3SO_3 \cdot CH_3CN$ (N–H···O bond, N···O = 2.830(3) Å [3]).

The remainder of the structure of the title compound is built up from a tetrahedral $[Zn(Br,Cl)_4]^{2-}$ anion, hydrogen bonded to a $[Et_3N(2)H]^+$ cation (Fig. 1). According to site occupation refinement, about 30(1)% of the halogen atoms of $[Zn(Br,Cl)_4]^{2-}$ are Cl (see preparation). Note however that Br by Cl substitution in the Ru complex, if present at all, must not exceed a few percent. The mean value of the Zn-(Br,Cl) bond lengths is 2.392 Å, by 0.02 Å shorter than for the $ZnBr_4$ tetrahedra in $MnZnBr_4 \cdot 6H_2O$ [4] or $MgZnBr_4 \cdot 7H_2O$ [5]. This bond length reduction corresponds well with what has to be expected from a comparison of $ZnBr_4$ and $ZnCl_4$ tetrahedra (characteristic bond lengths: Zn–Br = 2.41 Å [4, 5] Zn–Cl = 2.25 Å [6]) taking into account both the 2:1 ratio in the scattering powers of Br and Cl and the site occupation (70% Br, 30% Cl) determined by X-ray refinement.

The $[Et_3N(2)H]^+$ cation is disordered, its N atom being splitted into two approximately half occupied positions N(2a) and N(2b). Both atoms exhibit roughly pyramidal coordinations by the carbon atoms C(22), C(24), and C(26), but the apices of the C_3N pyramids point in opposite directions, in both cases toward Br. In this way, nitrogen N(2) is able to form alternatively a hydrogen bond to one of two adjacent $ZnBr_4$ tetrahedra: either N(2a)$\cdots$Br(4) = 3.28(2) Å or N(2b)$\cdots$Br(5) = 3.48(2) Å. Comparable N$\cdots$Br hydrogen bond distances were found for the numerous amine hydrobromides included in the Cambridge Crystallographic Database. The carbon atoms of this Et_3N molecule showed in part rather diffuse *Fourier* peaks and gave large and highly anisotropic displacement parameters upon refinement. From these observations one must conclude that the X-ray positions given in Table 1 represent averages of two superimposed molecules with differing atomic coordinates. Since it was not possible to resolve this superposition, the geometric parameters for [Et_3N(2a/2b)H]$^+$ are poor and have been omitted from Table 2.

The constituents of the title compound are arranged in the unit cell in a layer-like fashion parallel to (001) as shown in Fig. 3. Starting at $z = 0$ and ending at $z = 1$, the following layers are encountered consecutively: [Et_3N(2)H]$^+$, [$ZnBr_4$]$^{2-}$, [Et_3N(1)H]$^+$, 2 Ru(η^5-C_5Me_5)(η^4-C_5H_4O)Br, [Et_3N(1)H]$^+$, [$ZnBr_4$]$^{2-}$, and [Et_3N(2)H]$^+$. This stacking principle involves a separation of the hydrophilic parts of the structure near $z \sim 0$ from more hydrophobic parts (Ru complexes) near $z \sim 1/2$. The situation is comparable to the structure of Ru(η^5-C_5Me_5)(η^4-C_5H_4O)Br$\cdot$2H_2O [2], where double layers of Ru complexes alternate with layers of water molecules into which the cyclopentadienone oxygen atoms intrude to take part in two-dimensional H-bond networks.

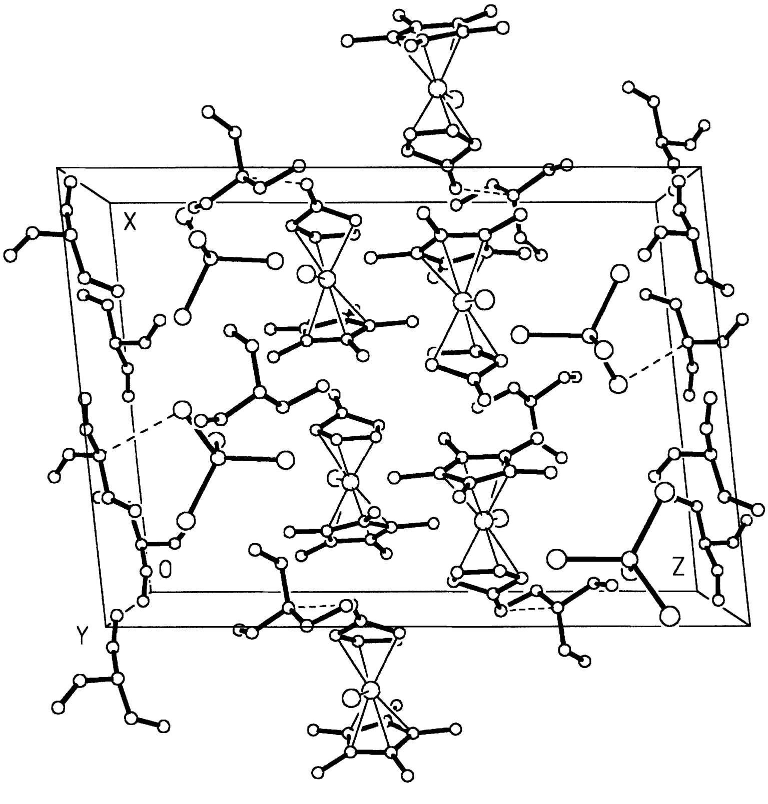


Fig. 3. Packing diagram of Ru(η^5-C_5Me_5)(η^4-C_5H_4O)Br$\cdot$2[Et_3NH]$\cdot$[Zn(Br,Cl)$_4$]

It appeared interesting to learn whether addition compounds related to the title compound might exist. An extensive search in the Cambridge Crystallographic Database (April 1998 release) revealed only three compounds showing comparable features. They all are larger neutral polyazamacrocyclic Ni complexes with formally co-crystallized $[Et_3NH]ClO_4$ [7, 8, 9], where Et_3N was applied in larger quantities in the syntheses as proton scavenger or as a nucleophile that supported isomerization [9]. A family of less related compounds are the salts $[MX_2(H_2O)_2] \cdot [Me_3NH] \cdot X$ (M = Mn, Fe, Co, Ni, Cu, Zn; X = Cl, Br) [10] where the trimethylammonium cations are weakly hydrogen bonded to the O atoms of the $[MX_2(H_2O)_2]$ octahedral chains, but not to the separate X anion.

Experimental

Synthesis

The reaction shown in Scheme 1 has been performed as a one-pot synthesis in CH_2Cl_2 at room temperature. As indicated by ^1H NMR spectroscopy, this path yielded the expected complex $Ru(\eta^5\text{-}C_5Me_5)(\eta^4\text{-}C_5H_4O)Br$ in solution. Upon crystallization, however, an unexpected solid was formed due to the following complications: The reduction of $[Ru(\eta^5\text{-}C_5Me_5)Br_2]_2$ (step 1) was performed with an excess of Zn (*ca.* 15 equiv), leading to the formation of $[Ru(\eta^5\text{-}C_5Me_5)Br]_4$ and a mixture of zinc chloride and zinc bromide. The origin of the chloride remains obscure, stemming either from the solvent (CH_2Cl_2) or an incomplete metathesis of $[Ru(\eta^5\text{-}C_5Me_5)Cl_2]_2$ with KBr used to obtain the starting compound of Scheme 1. After removal of the solid materials, 4-bromo-2-cyclopentene-1-one (4 equiv.) was added affording the Ru(IV)-η^3-cyclopentenoyl complex $Ru(\eta^5\text{-}C_5Me_5)(\eta^3\text{-}C_5H_5O)Br_2$ (step 2). Upon addition of NEt_3 (1.2 equiv), the brown solution turned dark red due to formation of $Ru(\eta^5\text{-}C_5Me_5)(\eta^4\text{-}C_5H_4O)Br$ (step 3). Crystallization by means of diethyl ether diffusion resulted in the formation of large red plates of the title compound reaching up to 2 mm in lateral dimensions and about 0.1 mm in thickness.

Crystal structure determination

Crystal data: $C_{27}H_{51}Br_{3.75}Cl_{1.25}N_2ORuZn$ (idealized), $FW = 930.11$, monoclinic, space group $P2_1/a$ (No. 14), $a = 14.307(2)$ Å, $b = 12.819(2)$ Å, $c = 19.897(4)$ Å, $\beta = 95.98(1)^\circ$, $V = 3629.3(11)$ Å^3, $Z = 4$, $T = 295(2)$ K, $\lambda = 0.71073$ Å, $d_{calc} = 1.702$ mg/mm^3, $\mu = 5.32$ mm^{-1}. A red plate of the title compound ($0.096 \times 0.35 \times 0.42$ mm) was used for data collection with a PHILIPS PW1100 four-circle diffractometer and graphite monochromatized MoK_α radiation. Cell dimensions were determined from $\pm\omega$ scans of 20 reflections ($\theta = 15$–19°). The intensities of 5299 reflections with $\theta < 23^\circ$, $-15 \leq h \leq 15$, $0 \leq k \leq 14$, $0 \leq l \leq 21$ were measured by $\theta - 2\theta$ – scans using scan widths of $1.0^\circ + 0.33^\circ \tan(\theta)$ and a scan speed of $3^\circ \cdot \min^{-1}$. Three standard reflections monitored every two hours showed a small decline in intensities (max. 2.5%). The data were corrected for Lp, crystal decay, and for absorption (*Gaussion* integration, transmission factors 0.18–0.60) Removal of systematic extinctions yielded 5026 unique reflections.

The structure was solved by direct methods. Structure refinement of F^2 was carried out with the program SHELXL93 [11]. Anisotropic temperature factors were applied for all non-hydrogen atoms. The hydrogen atoms were inserted in calculated positions and refined riding with the atoms to which they were bonded using isotropic temperature factors fixed at $1.2 \times U_{eq}$ ($1.5 \times$ for CH_3 groups) of their carrier atoms. Orientational disorder of one triethylammonium nitrogen atom and mixed site occupation for the halogen atoms of the $[Zn(Br,Cl)_4]^{2-}$ anion were taken into account. The presence of chlorine was established *via* a qualitative electron microprobe analysis. The final full-matrix least-squares refinement varied 335 parameters and used 5026 independent reflections weighted by $w = 1/(\sigma^2(F_o^2) + (0.05P)^2 + 5.5P)$ where $P = (F_o^2 + 2F_c^2)/3$. Final $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.075$, $wR_2 = (\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma(w(F_o^2)^2))^{1/2} = 0.102$, $S = 1.02$ for all data; $R_1 = 0.044$ of the 3633 reflections with $F_o > 4\sigma(F_o)$. The final difference *Fourier* map showed minimum and maximum values of -0.53 and $0.76\,e \cdot \text{Å}^{-3}$ with most prominent features near $[Zn(Br,Cl)_4]^{2-}$. Atomic positional parameters are presented in Table 1, bond lengths and angles in Table 2. Additional material to the structure determination may be obtained from Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D76344 Eggenstein-Leopoldshafen, Germany, referring to the deposition number CSD-410168, the names of the authors, and the citation of the present paper.

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