

Hexakis(acetonitrile)ruthenium(II) tetrachlorozincate
2.55-hydrateAtilio Anzellotti* and Alexander
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Key indicators

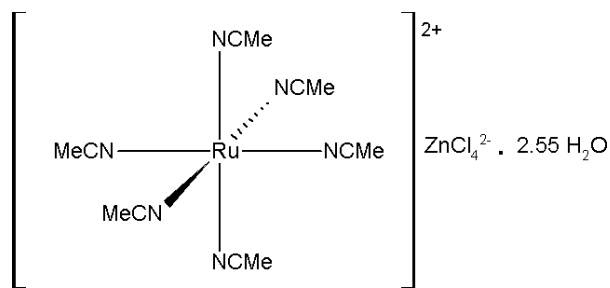
Single-crystal X-ray study
T = 293 K
Mean $\sigma(\text{C}-\text{C}) = 0.012 \text{ \AA}$
H-atom completeness 78%
Disorder in solvent or counterion
R factor = 0.058
wR factor = 0.157
Data-to-parameter ratio = 17.6For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

The crystal structure of the title compound, $[\text{Ru}(\text{CH}_3\text{CN})_6][\text{ZnCl}_4] \cdot 2.55\text{H}_2\text{O}$, consists of $[\text{Ru}(\text{CH}_3\text{CN})_6]^{2+}$ units (with the Ru atom in a slightly distorted octahedral environment coordinated by six acetonitrile ligands) and $[\text{ZnCl}_4]^{2-}$ moieties (with the Zn atom in a distorted tetrahedral environment). The Ru atom and one of the Zn—Cl bond axes lie on the threefold axis, the N—Ru—N angles are 89.2 (2) and 90.3 (2)°, and the Cl—Zn—Cl angles are 111.42 (6) and 107.44 (6)°.

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Comment

Homoleptic complexes of Ru^{II} with labile ligands, such as H_2O (Bernhard *et al.*, 1982), DMF (Judd *et al.*, 1995) or CH_3CN , are of great interest from the synthetic point of view, since a complete modification of the coordination sphere can be achieved through substitution with less labile ligands. These homoleptic complexes constitute an attractive alternative to the common starting material $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ which is a heterogeneous, ill-defined mixture of variable oxidation-state, oxochloro and hydroxochloro, monomeric and polymeric ruthenium complexes, where the average oxidation state of the material is closer to Ru^{IV} than it is to Ru^{III} (Seddon & Seddon, 1984). In addition, the product obtained from $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ reduction usually retains Cl as a ligand with a relatively inert Ru—Cl bond, which can be undesirable for certain applications (Gilbert *et al.*, 1970; Evans *et al.*, 1973). Previous studies (Schrock *et al.*, 1974) reported the synthesis



(I)

of $[\text{Ru}(\text{CH}_3\text{CN})_6][\text{BF}_4]_2$ from $[\text{Ru}(\pi\text{-C}_3\text{H}_5)_2(\text{norbornadiene})]$ in a two-step process, but no crystal structure was presented. Two other compounds with the $[\text{Ru}(\text{CH}_3\text{CN})_6]^{2+}$ cation are known, *viz.* the $[\text{Ru}(\text{CH}_3\text{CN})_6][7-(\eta^6\text{-C}_6\text{Me}_6)\text{-nido-7-RuB}_{10}\text{H}_{13}]_2$ complex (Brown *et al.*, 1987) and the $[\text{Ru}(\text{CH}_3\text{CN})_6][(\text{C}_7\text{H}_7\text{O}_3\text{S})_2] \cdot 2\text{H}_2\text{O}$ complex (Luginbühl *et al.*, 1989). We report here the structure of a homoleptic complex, (I), which was obtained by reduction of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ with zinc

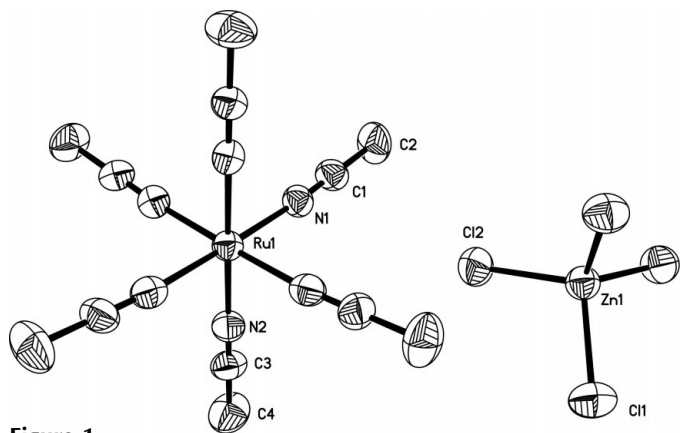


Figure 1
The molecular structure of the homoleptic complex (I) showing the atom-numbering scheme and 50% probability displacement ellipsoids. Water molecules are not shown.

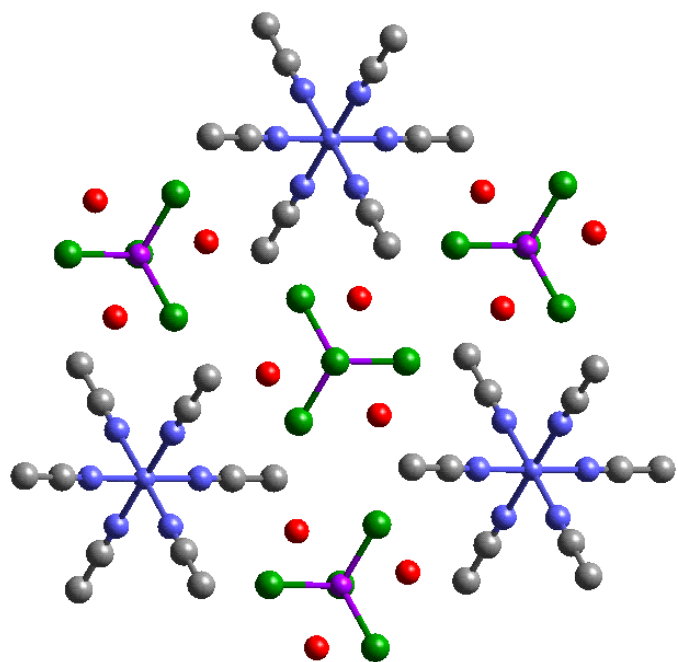


Figure 2
Projection of the homoleptic complex (I) in the *ab* plane showing the water solvate molecule OW1. The OW2 and OW3 water molecules are located along the threefold axis, and are overlapped by the Cl atom.

powder in acetonitrile and further controlled recrystallization. Interestingly, the reaction yield can be improved up to 70% by addition of ZnCl_2 to the recrystallization mixture (see *Experimental*). This fact along with the presence of tetrakis-(acetonitrile)dichlororuthenium(II) in the mother liquor, evidenced by ^1H NMR and IR measurements (Fogg *et al.*, 1995), leads us to think of the involvement of an equilibrium between the $[\text{Ru}(\text{CH}_3\text{CN})_6][\text{ZnCl}_4]$ and $\text{RuCl}_2(\text{CH}_3\text{CN})_4$ species.

The structure of (I) consists of discrete $[\text{Ru}(\text{CH}_3\text{CN})_6]^{2+}$ cationic units and $[\text{ZnCl}_4]^{2-}$ anions along with crystallization water molecules (Fig. 1). The Ru1 atom is located in special position $6c$ (0,0,*z*) in the unit cell, showing a threefold

symmetry (Fig. 2). The $\text{Ru}(\text{CH}_3\text{CN})_6^{2+}$ cation orientation, toward the *z* axis, results in only two acetonitrile molecules being crystallographically independent. The Ru^{II} atom exhibits a slightly distorted octahedral coordination, with $\text{N1}-\text{Ru1}-\text{N1}$ angles of $89.2(2)^\circ$ and $\text{N1}-\text{Ru1}-\text{N2}$ angles of $90.3(2)^\circ$, $\text{Ru1}-\text{N1}$ bond distances of $2.026(6) \text{ \AA}$ and $\text{Ru1}-\text{N2}$ bond distances of $2.033(6) \text{ \AA}$. The coordinated acetonitrile molecules are linear [angles: $\text{N1}-\text{C1}-\text{C2}$ $179.5(9)^\circ$ and $\text{N2}-\text{C3}-\text{C4}$ $179.8(11)^\circ$], but slightly bent with respect to the Ru atom [angles: $\text{Ru1}-\text{N2}-\text{C3}$ $175.3(6)^\circ$ and $\text{Ru1}-\text{N1}-\text{C1}$ $176.1(6)^\circ$]. The resulting single signal for the equivalent acetonitriles in the ^1H NMR spectra indicates the octahedral coordination of the Ru atom. The $[\text{ZnCl}_4]^{2-}$ anion has a distorted tetrahedral geometry, with angles $\text{Cl2}-\text{Zn1}-\text{Cl1}$ $107.44(6)^\circ$ and $\text{Cl2}-\text{Zn1}-\text{Cl2}$ $111.42(6)^\circ$, and bond distances $\text{Zn1}-\text{Cl1}$ $2.293(4) \text{ \AA}$ and $\text{Zn1}-\text{Cl2}$ $2.259(2) \text{ \AA}$. Atoms Zn1 and Cl1 are also located in special position $6c$ (0,0,*z*) in the unit cell with the $\text{Zn1}-\text{Cl1}$ bond parallel to the *c* axis making two Cl atoms independent. Values found for bond distances and angles are consistent with those of previously reported complexes with the same $[\text{Ru}(\text{CH}_3\text{CN})_6]^{2+}$ cation or $[\text{ZnCl}_4]^{2-}$ anion.

Data retrieved from the April 2001 version (5.21) of the Cambridge Structural Database (Allen & Kennard, 1993; 233 218 entries) for analogous compounds of the type $[\text{M}(\text{CH}_3\text{CN})_6][\text{ZnCl}_4]$, where *M* is a transition metal, afforded the complexes with Ni^{II} (Søtøfte *et al.*, 1976) and V^{II} (Chandrasekhar & Bird, 1985). These complexes crystallized in the triclinic space group $P\bar{1}$, while (I) has a higher symmetry (space group $R\bar{3}$).

Experimental

The synthesis of (I) was carried out under N_2 by refluxing a solution of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ (261.42 mg, 1 mmol) with zinc powder (130.71 mg, 2 mmol) in stirred acetonitrile for 2 h. The resulting mixture was vacuum filtered and the yellow solution evaporated. The yellow solid was then redissolved in a methanol/acetonitrile (1:2) mixture. Addition of a few drops of diluted HCl provided, on standing for *ca* 4 d, light-yellow crystals suitable for X-ray analysis (yield 36%); importantly the yield can be improved by addition of ZnCl_2 in a 1:4 (Zn/Ru) ratio. IR (KBr, cm^{-1}): (*br*, O–H) 3500, (*s*, $\text{C}\equiv\text{N}$) 2325, 2296, (*s*, C–H) 2975, 2911. ^1H NMR (D_2O): $\delta = 2.43$ (*s*). IR spectra were recorded in a Nicolet Magna-IR 560 spectrometer. ^1H NMR spectra were recorded in a Bruker 300 MHz spectrometer. Calculated for $\text{C}_{12}\text{N}_6\text{H}_{23.1}\text{RuZnCl}_4\text{O}_{2.55}$: C 23.96, N 13.98, H 3.84%; found: C 23.99, N 13.95, H 3.51.

Crystal data

$[\text{Ru}(\text{C}_2\text{H}_3\text{N})_6][\text{ZnCl}_4] \cdot 2.55\text{H}_2\text{O}$
 $M_r = 600.50$
 Trigonal, $R\bar{3}$
 $a = 11.7436(17) \text{ \AA}$
 $c = 30.932(8) \text{ \AA}$
 $V = 3694.4(12) \text{ \AA}^3$
 $Z = 6$
 $D_x = 1.619 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation
 Cell parameters from 20 reflections
 $\theta = 26.5\text{--}36.7^\circ$
 $\mu = 2.04 \text{ mm}^{-1}$
 $T = 293(2) \text{ K}$
 Prism, light yellow
 $0.32 \times 0.20 \times 0.14 \text{ mm}$

Data collection

Rigaku AFC-7S diffractometer	$R_{\text{int}} = 0.023$
ω -2 θ scans	$\theta_{\text{max}} = 25.0^\circ$
Absorption correction: ψ scan (North <i>et al.</i> , 1968)	$h = -12 \rightarrow 12$
$T_{\text{min}} = 0.650$, $T_{\text{max}} = 0.751$	$k = 0 \rightarrow 13$
1601 measured reflections	$l = 0 \rightarrow 36$
1461 independent reflections	3 standard reflections
1033 reflections with $I > 2\sigma(I)$	every 150 reflections
	intensity decay: none

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.058$	$w = 1/[\sigma^2(F_o^2) + (0.1002P)^2]$
$wR(F^2) = 0.157$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.02$	$(\Delta/\sigma)_{\text{max}} = 0.001$
1461 reflections	$\Delta\rho_{\text{max}} = 2.93 \text{ e } \text{Å}^{-3}$
83 parameters	$\Delta\rho_{\text{min}} = -0.50 \text{ e } \text{Å}^{-3}$

Table 1
Selected geometric parameters (Å, °).

Ru1—N1	2.026 (6)	Cl2—Zn1	2.2590 (19)
Ru1—N2	2.033 (6)	Zn1—Cl1	2.293 (4)
N1 ⁱ —Ru1—N1	89.2 (2)	C3—N2—Ru1	175.3 (6)
N1 ⁱ —Ru1—N2	90.3 (2)	N1—C1—C2	179.5 (9)
N1 ⁱⁱ —Ru1—N2	178.3 (2)	N2—C3—C4	179.8 (11)
N1—Ru1—N2	89.2 (2)	Cl2 ⁱⁱⁱ —Zn1—Cl2	111.42 (6)
N2 ⁱ —Ru1—N2	91.3 (2)	Cl2—Zn1—Cl1	107.44 (6)
Cl1—N1—Ru1	176.1 (6)		

Symmetry codes: (i) $-x + y, 1 - x, z$; (ii) $1 - y, 1 + x - y, z$; (iii) $1 - y, x - y, z$.

The water molecules in the framework are disordered and were located in three positions with different occupation factors. This disorder was modelled, in an interactive fashion, by occupation factor and displacement parameters. In the interactive procedure chosen to optimize the refinement, we found that the best option was to fix U_{iso} of OW2, otherwise the U_{iso} parameters of the other molecules were greatly affected. The water H atoms were not included. Occupation factors of 0.57 (2), 0.29 (4) and 0.55 (4) were obtained for OW1, OW2 and OW3, respectively. Stoichiometry calculations for water molecules based on occupation factors resulted in a value of 2.55, which is consistent with the elemental analysis.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1992); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXL97*; software used to prepare material for publication: *SHELXL97*.

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