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The rhodium(III) trisacetonitrile complexes: a re-investigation of the synthesis of *fac*- and *mer*-[$RhCl_3(CH_3CN)_3$], their characterization by 2D NMR spectroscopy and the X-ray crystal structure of *mer*-[$RhCl_3(CH_3CN)_3$]·CH_3CN ☆

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Abstract

It is shown that the reaction of $RhCl_3 \cdot 3H_2O$ with acetonitrile normally produces mixtures of *mer*- and *fac*-[$RhCl_3(CH_3CN)_3$] (**1a** and **1b**, respectively). The IR and ^1H NMR spectra of these isomers were re-investigated. Their two-dimensional (^{103}Rh,^1H) NMR spectra were also recorded. Equilibrium and exchange studies of **1a** and **1b** in CD_3CN were performed. It was found that in **1a** the exchange rate of the nitrile molecule *trans* to Cl is much faster than those of mutually *trans* nitriles. Also the nitrile molecules in **1b** underwent fast exchange in CD_3CN; however, their rate was slightly faster than that of the more labile CH_3CN in **1a**. The X-ray crystal structure of *mer*-[$RhCl_3(CH_3CN)_3$]·CH_3CN (**1c**) was determined. Crystal data: triclinic space group $P\bar{1}$, $a=12.200(10)$, $b=12.227(10)$, $c=12.270(11)$ Å, $\alpha=115.95(7)$, $\beta=101.52(7)$, $\gamma=102.93(6)°$, $V=1509(2)$ Å^3, $Z=4$.

Keywords: Rhodium complexes; Crystal structures; Acetonitrile complexes; *fac–mer* isomerism; ^{103}Rh NMR spectroscopy

1. Introduction

Compounds of the general formula MX_nL_{6-n} are useful starting materials for the preparation of mononuclear metal halide complexes, when the L ligands are readily displaced. Well known examples of compounds of this type are the tetrahydrofuran [1], dimethyl sulfoxide [2] and acetonitrile complexes of the transition metals [3]. Although more than a dozen transition-metal complexes of the type [$MCl_3(CH_3CN)_3$] are known, structural studies, particularly of their *fac* and *mer* isomers, are rather limited as only the Ti(III) and Mo(III) complexes have been crystallographically characterized [4,5].

Organonitrile complexes of Rh(III) were first described in the mid-sixties [6,7] and the synthesis and characterization by IR and ^1H NMR spectroscopy of *mer*-[$RhCl_3(CH_3CN)_3$] (**1a**) [7,8] and *fac*-[$RhCl_3(CH_3CN)_3$] (**1b**) [8,9] were reported soon after. Compounds of this composition have been extensively used in this laboratory as starting materials for the preparation of trispyrazolylborate complexes of rhodium [10]. However, during these studies difficulties were experienced with the preparation of **1b** using the method reported in the literature [8]: although the compounds obtained gave satisfactory elemental analyses, their spectroscopic data did not agree with those reported for this compound and often differed from sample to sample. This paper reports a re-investigation of the reaction of $RhCl_3 \cdot 3H_2O$ with CH_3CN and presents an NMR study of the samples obtained by varying the reaction conditions. In addition, the X-ray structure of *mer*-[$RhCl_3(CH_3CN)_3$]·CH_3CN (**1c**) is reported.

Interesting information about trisacetonitrile complexes, particularly those of vanadium and titanium, was obtained by equilibrium and exchange studies in solution: acetonitrile solutions of VCl_3 were shown to contain [$VCl_3(CH_3CN)_3$] [11] and ^1H NMR studies of the temperature dependence of the linewidth established the presence of two distinct exchange processes [12–14], as found in the related Ti system [15,16]. Although the IR spectrum of solid

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☆ Dedicated to Professor Dr Fred Basolo on the occasion of his 75th birthday.

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$[VCl_3(CH_3CN)_3]$ indicated that its geometry is facial [17], it was suggested that only the *mer* isomer is present in solution, and that the CH_3CN ligands *trans* to chloride exchange more rapidly ($k=8.2\times10^5$ s^{-1}) than those *trans* to other CH_3CN molecules ($k=7.9\times10^2$ s^{-1}) [12]. It was also noted that the magnitude and sign of the $\Delta S^{\neq}$ values for the exchange process for these two types of acetonitrile, in deuterated CD_3NO_2, are surprisingly different (+26 and −28 J K^{-1} mol^{-1}, respectively) [12,14]. This led O'Brien to propose an alternative explanation for this behavior, i.e. that both the facial and meridional isomers are present in solution [13] and that the two processes observed are due to their exchanging at different rates.

The $[VCl_3(CH_3CN)_3]$ system was, therefore, extensively studied and extended Hückel MO calculations were carried out [18]. From these calculations it was concluded that, in *mer*-$[VCl_3(CH_3CN)_3]$, the V–N bonding of the unique nitrile differs significantly from that of the other two. Furthermore, this difference is larger than that between the labile nitriles in the *mer* and *fac* isomers. Therefore, the observation of two exchange processes could be accounted for without having to assume that also the *fac* isomer is present in solution. However, the simultaneous formation of both isomers was still considered likely.

To obtain more information about the dynamics of nitrile exchange in complexes of this type of ligand, exchange studies were carried out for the corresponding rhodium(III) species **1a** and **1b** and are reported here.

2. Experimental

2.1. Syntheses

All solvents, of puriss. p.a. quality, and CD_3CN, were purchased from Fluka, while CD_3NO_2 was obtained from ARMAR AG, Döttingen, Switzerland. $Na_3[RhCl_6]\cdot12H_2O$ and $RhCl_3\cdot3H_2O$ were purchased from Fluka and Johnson Matthey & Brandenberger AG, Zürich, Switzerland, respectively.

2.2. Attempted synthesis of pure *fac*[$RhCl_3(CH_3CN)_3$] (1b)

(i) *Using the method of Catsikis and Good [8].* 1.7 g (6.45 mmol) $RhCl_3\cdot3H_2O$ were dissolved in 250 ml CH_3CN, the solution brought to boiling and kept at this temperature for 1 min. During this time the solution underwent a color change, from red to orange, not reported in the literature. The solution was cooled to r.t., the volume reduced to 10 ml and the product precipitated with ether. The solid, after filtration, was taken up in 20 ml CH_3CN and the product reprecipitated with ether. *Anal.* Calc. for $C_6H_9N_3Cl_3Rh$: C, 21.68; H, 2.73; N, 12.64; Cl, 31.99. Found: C, 21.96; H, 2.88; N, 12.58; Cl, 32.00%. The ^1H NMR spectrum of this material showed that it consisted of a 3:1 mixture of **1a** and **1b**.

(ii) *Using a lower reaction temperature.* The reaction was carried out as above, but the solution was warmed only (~40 °C) until the color change occurred. Further work-up was as described above. *Anal.* Found: C, 21.63; H, 2.85; N, 12.45; Cl, 32.21%. This material proved to be a 5:1 mixture of **1a** and **1b**.

(iii) *Using a stoichiometric amount of CH_3CN in an r.t. reaction.* 200 mg (0.76 mmol) $RhCl_3\cdot3H_2O$ were dissolved in 3 ml isopropanol and 0.6 ml water added. The solution was stirred for 30 min and then a stoichiometric amount of CH_3CN (0.012 ml) was added. The mixture was stirred for 1 day. The yellow–orange precipitate deposited during this period was filtered off, washed with ether and dried under high vacuum. The material was found to be the pure *mer* isomer **1a**. IR (cm^{-1}): 2973 s, 2915 s (CH str); 2327 s (C≡N str); 1407 s, 1357 s (CH_3 def); 1025 s (CH_3 rock); 954 m (C–C str); 453 s; 350 s (Rh–Cl str).

(iv) *Using $Na_3[RhCl_6]$.* 100 mg (0.16 mmol) $Na_3[RhCl_6]\cdot12H_2O$ were dissolved in 25 ml H_2O and the solution was stirred for 1 day at room temperature. To this pale yellow solution 2 ml CH_3CN were then added and the yellow product was precipitated with ether after 2 h. This material was found also to be a mixture of **1a** and **1b** (~2:1).

Air-stable red–orange crystals of *mer*-$[RhCl_3(CH_3CN)_3]\cdot CH_3CN$ (**1c**), suitable for X-ray diffraction, were obtained as follows. A mixture of **1a** and **1b** in CH_3CN and the trispyrazolylborate $Na[HB(3,5\text{-}(CF_3)_2\text{-}pz)_3]$ [10] were refluxed for 12 h. Crystals of **1c** formed from this solution after storage at room temperature for one week. IR (cm^{-1}): 2326 s, 2251 sh, 2234 s (C≡N str), 2101 s; 441 s; 343 (Rh–Cl str); CH str not observed.

2.3. Measurements

C, H, N and Cl microanalyses were performed by the Microanalytical Laboratory of the ETH Zürich.

IR spectra were recorded as KBr pellets on a Perkin-Elmer model 883 spectrophotometer. ^1H NMR spectra and two-dimensional HMQC (^{103}Rh,^1H) NMR spectra were recorded on Bruker AC 200 and AMX 500 spectrometers. The chemical shift scales are relative to internal TMS (^1H) and $\Xi=3.16$ MHz (^{103}Rh).

2.4. Crystallography

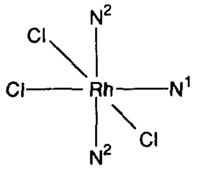
A prismatic red–orange crystal of **1c**, of size 0.5×0.35×0.3 mm, mounted on a glass fiber, was used for the structure determination. Details of the X-ray data collection are as follows: $C_8H_{12}N_4Cl_3Rh$, $M=373.5$, triclinic, space group $P\bar{1}$, $a=12.200(10)$, $b=12.227(10)$, $c=12.270(11)$ Å, $\alpha=115.95(7)$, $\beta=101.52(7)$, $\gamma=102.93(6)°$, $V=1509(2)$ Å^3, $Z=4$, $\mu=1.644$ mm^{-1}, $T=293$ K, $F(000)=736$, $D_c=1.644$ Mg m^{-3}; Picker-STOE diffractometer, graphite crystal monochromated Mo Kα radiation (0.71073 Å) and ω-scan mode. Accurate unit-cell parameters were obtained by least-squares fits of the 2θ values of 25 high order reflections. A total of 2819 independent reflections ($3.0 < 2\theta < 40.0°$) was collected with index ranges $-11 \leqslant h \leqslant 11$, $-11 \leqslant k \leqslant 10$ and $0 \leqslant l \leqslant 11$. These gave 2607 observed ($F > 4.0\sigma(F)$) reflections. No absorption correction was applied.

The structure was solved by a combination of Patterson and Fourier methods [19] and refined by full-matrix least-squares (289 parameters, the function minimized was $[\Sigma w(F_o - F_c)^2]$), with anisotropic thermal ellipsoids for all non-hydrogen atoms. Extinction corrections were deemed to be unnecessary. The hydrogen atoms were introduced into the calculated positions with a riding model with fixed isotropic U. The final values $R = 0.0503$, $R_w = 0.0758$, $GOF = 0.49$ for 289 variables, with weighting scheme $w^{-1} = \sigma^2(F) + 0.0257(F)^2$ were obtained. Maximum and minimum peaks were 1.29 (located on Rh) and −1.15 e Å^{-3}; largest and mean $\Delta/\sigma = 0.115$ and 0.014. The final coordinates and U_{eq} values are listed in Table 1. See also Section 5.

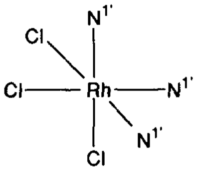
3. Results and discussion

The reaction of $RhCl_3 \cdot 3H_2O$ with CH_3CN, using the conditions described by Catsikis and Good [8], gave as reported, a yellow material. This was characterized by elemental analysis, in addition to IR and ^{1}H NMR spectroscopy.

The six-coordinate, uncharged $[RhCl_3(CH_3CN)_3]$ can exist either as a *mer* or a *fac* isomer, **1a** and **1b**, having C_{2v} and C_{3v} symmetry, respectively. The former should normally give rise to one strong and two weak ν(Rh–Cl) stretching vibrations while in the latter only two corresponding bands, in general one strong and the other of medium intensity, are expected in the IR spectrum.



1a



1b

Catsikis and Good [8] assigned a *fac* geometry **1b** to the product obtained by this procedure as it showed two strong ν(Rh–Cl) bands at 356 and 346 cm^{-1} in the IR spectrum. These authors also reported the preparation of the *mer* isomer which showed three IR bands at 356, 350 and 300 cm^{-1}.

Earlier Johnson and Walton [7] obtained, upon warming $RhCl_3 \cdot 3H_2O$ with an excess of CH_3CN, a product which was formulated as **1a** as it showed bands at 350, 340 and 300 (sh) cm^{-1}. Walton [20] repeated this preparation and reformulated his product as **1b** because it showed only one band at 350 cm^{-1} with the possibility of an ill-defined shoulder at ~355 cm^{-1}.

Interestingly, in the sample of $[RhCl_3(CH_3CN)_3]$ obtained by method (i) during this study only one ν(Rh–Cl) stretching mode at 350 cm^{-1} was observed.

Table 1
Atomic coordinates (×10^4) and equivalent isotropic displacement coefficients (Å^2×10^3)

	x	y	z	U_{eq} [a]
Rh(1)	1847(1)	2596(1)	3471(1)	43(1)
Rh(2)	3633(1)	1467(1)	8302(1)	43(1)
Cl(1)	583(1)	452(2)	1973(2)	61(1)
Cl(2)	2309(1)	2008(2)	4989(2)	54(1)
Cl(3)	3115(1)	4738(1)	4952(2)	62(1)
Cl(4)	3796(1)	3273(2)	10204(2)	60(1)
Cl(5)	5455(1)	1472(2)	9281(2)	55(1)
Cl(6)	3394(2)	−350(4)	6376(2)	65(1)
N(1)	496(5)	2978(4)	4027(5)	52(3)
N(2)	1435(4)	3097(5)	2127(6)	55(3)
N(3)	3220(5)	2263(4)	2952(5)	48(3)
N(4)	4455(4)	2596(5)	7709(5)	47(3)
N(5)	2003(5)	1452(4)	7441(5)	48(3)
N(6)	2832(5)	295(5)	8865(5)	53(3)
N(7)	2043(10)	7057(12)	2076(15)	181(10)
N(8)	9011(9)	4671(11)	2172(12)	179(8)
C(1)	−256(6)	3173(6)	4401(6)	54(3)
C(2)	−1237(7)	3464(8)	4792(10)	96(5)
C(3)	1191(5)	3331(6)	1325(7)	56(4)
C(4)	875(7)	3623(8)	310(7)	78(5)
C(5)	4037(6)	2170(5)	2664(5)	44(3)
C(6)	5137(5)	2118(6)	2361(6)	56(3)
C(7)	4901(5)	3166(6)	7300(6)	51(3)
C(8)	5440(6)	3883(7)	6753(7)	70(4)
C(9)	1111(6)	1442(5)	6969(5)	47(3)
C(10)	8(6)	1414(7)	6380(7)	72(4)
C(11)	2368(5)	−368(6)	9175(6)	48(3)
C(12)	1752(6)	−1200(6)	9543(6)	60(4)
C(13)	2621(9)	8068(11)	2655(11)	111(7)
C(14)	3237(9)	9261(9)	3234(9)	96(6)
C(15)	8141(8)	4795(8)	1958(9)	95(5)
C(16)	7056(7)	5017(8)	1700(10)	105(6)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

The structure of each isomer can also be assigned by ^{1}H NMR spectroscopy as *mer*-$[RhCl_3(CH_3CN)_3]$ (**1a**) contains two non-equivalent CH_3CN, N^1 and N^2, in a ratio 1:2, in contrast to *fac*-$[RhCl_3(CH_3CN)_3]$ (**1b**) where these donors N$^{1'}$ are all equivalent. Thus Catsikis and Good [8] report that the sample which had been assigned *fac* geometry on the basis of their IR spectra showed only one signal at 2.60 ppm (CD_3CN), different from the δ values of 2.64 and 2.59 for the samples to which they assigned structure **1a**. Therefore, the ^{1}H NMR spectroscopic characterization of *fac*-$[RhCl_3(CH_3CN)_3]$ (**1b**) seemed unambiguous. However, it should be noted that these spectra were recorded at 60 MHz.

Freshly prepared samples of the material prepared in this laboratory, obtained using the description given by these authors [8] which, as mentioned earlier, showed only one ν(Rh–Cl) band at 350 cm^{-1}, were also studied by ^{1}H NMR spectroscopy at 200 MHz. When CD_3CN was used as solvent, two signals were observed at 2.60 and 2.57 ppm, at times integrating to 2:1, consistent with the presence of *mer*-$[RhCl_3(CH_3CN)_3]$ (**1a**). To avoid problems with nitrile exchange, later NMR spectroscopic studies were performed

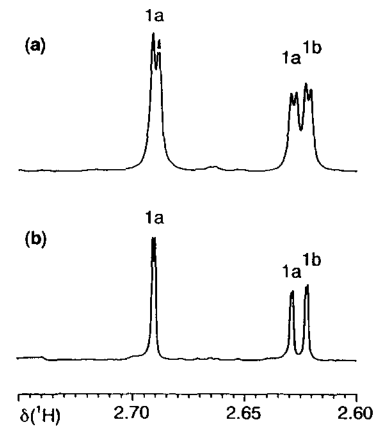


Fig. 1. The ^1H NMR spectrum of a sample containing a mixture of *mer*-[$RhCl_3(CH_3CN)_3$] (**1a**) and *fac*-[$RhCl_3(CH_3CN)_3$] (**1b**) in CD_3NO_2: (a) at 200 MHz; (b) at 500 MHz.

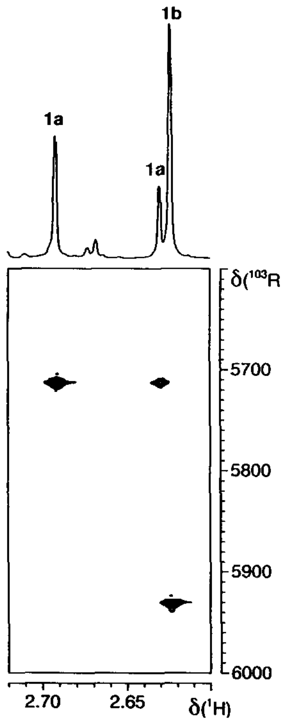


Fig. 2. ^{103}Rh–^1H heteronuclear correlation spectrum showing the mixture of *mer*-[$RhCl_3(CH_3CN)_3$] (**1a**) and *fac*-[$RhCl_3(CH_3CN)_3$] (**1b**) in CD_3NO_2.

in CD_3NO_2 because of its low coordinating power. The spectra of samples obtained by method (i), in this solvent, showed two signals at 2.69 and 2.62 ppm, in variable intensity ratios, which could reach 1:2. In addition, the signal at low field appeared as a doublet, while the signal at 2.62 ppm was sometimes poorly resolved.

High-field NMR spectroscopy finally revealed that the products obtained as described above are actually *mixtures* of the two isomers, **1a** and **1b**, in variable ratios. Fig. 1(a) shows the 200 MHz ^1H NMR spectrum of a mixture of **1a** and **1b**, while Fig. 1(b) shows the 500 MHz ^1H NMR spectrum of the same sample. In both cases the three CH_3CN resonances appear as doublets centered at 2.69, 2.63 and 2.62 ppm, the latter two corresponding to the unresolved resonance at 2.57 ppm in CD_3CN. The ^{103}Rh–^1H correlation spectra of a sample obtained by method (i), recorded in CD_3NO_2 at room temperature (Fig. 2), shows that the two signals at low-field, which are in a 2:1 ratio, can be assigned to **1a** and the other signal to **1b**. The $^4J(^1H,^{103}Rh)$ coupling constants for N^1 and N^2 of **1a** are 0.45 and 0.55 Hz, while it is 0.55 Hz in **1b**. The relevant NMR data are summarized in Table 2.

It is known that complex **1b** isomerizes to the more stable *mer* isomer **1a** upon refluxing in CH_3CN for 12 h [8,9]. The ^1H NMR spectrum of a mixture of **1a** and **1b**, treated as described by Catsikis and Good [8], showed that most of **1b** had isomerized to **1a**. Heating a mixture of **1a** and **1b** in nitromethane to see whether isomerization occurred also in this solvent, revealed the release of CH_3CN and the formation of numerous new, possibly multinuclear species, as 71 resonances between 2.9 and 2.6 ppm were found.

*Other attempts to synthesize fac-[$RhCl_3(CH_3CN)_3$] (**1b**).* To avoid the possible influence of the temperature and of excess of CH_3CN on the isomerization of **1b** to **1a**, a synthetic route similar to that reported for the very well characterized [$RhCl_3(DMSO)_3$] complexes [24,25] was followed. This method uses very mild reaction conditions, although this route [24] is known to yield the *mer* isomer. However, also in the case of CH_3CN this procedure yielded only pure **1a**. As aquation of $[RhCl_6]^{3-}$ produces *fac*-[$RhCl_3(H_2O)_3$] [26], in another attempt, $Na_3[RhCl_6]$ was used as a starting material and allowed to form *fac*-[$RhCl_3(H_2O)_3$] before adding CH_3CN. However, also this procedure gave a mixture of **1a** and **1b**.

*Equilibrium and exchange studies of **1a** and **1b** in CH_3CN solution.* The ^1H NMR spectrum at 500 MHz of a mixture of **1a** and **1b**, in a 3:1 ratio, in CD_3CN, after 2 h, showed three signals at 2.60, 2.57 and 2.00 ppm, the latter due to free CH_3CN, with relative integrals of 2:1.53:0.83. No $^4J(^1H,^{103}Rh)$ couplings were observed and the differentiation between the unique CH_3CN, N^1, of **1a** and those of **1b** was not possible in this spectrum. After 25 h the integration of the three signals gave a 2:0.48:2.12 ratio, and the doublet

Table 2
Selected NMR parameters of [$RhCl_3(CH_3CN)_3$] complexes **1a**–**1c**

Compound	δ(¹H) (ppm)	δ(¹⁰³Rh) [a] (ppm)	⁴J(¹H,¹⁰³Rh) (Hz)
1a	2.69 (6H)	5712	0.55
	2.63 (3H)		0.45
1b	2.62 (9H)	5930	0.55
1c	2.69 (6H)	5712	0.55
	2.63 (3H)		0.40
	2.00 (3H) [b]		

[a] Chemical shifts in CD_3NO_2 were measured at 293 K indirectly by two-dimensional methods [21–23] and are expressed relative to the absolute scale Ξ = 3.16 MHz.

[b] Cocrystallized acetonitrile.

(due to $^4J(^1H,^{103}Rh)$ coupling) of N^1 in **1a** was resolved, indicating that the $N^{1'}$ ligands had been completely replaced by CD_3CN. After 36 h the signal due to N^1 of **1b** had completely disappeared, i.e. these CH_3CN had completely exchanged against CD_3CN, and only the signal due to the two equivalent CH_3CN ligands N^2 in **1a** was present although its intensity had decreased ~80%. Thus the NMR spectra clearly reveal that their exchange rate is much slower than that of the same ligand *trans* to chloride. It also shows that the exchange rate of CH_3CN in *trans* positions to Cl in **1a** is slightly slower than that of their equivalents in **1b**. Thus, the use of high-field NMR spectroscopy in the rhodium system showed a further distinction between the two isomers, i.e. the presence of three different exchange rates. These results support the conclusions reached for the related vanadium system based on extended Hückel calculations [18].

Finally, if a CD_3CN solution of a mixture of **1a** and **1b** is left at room temperature for 3 days, due to the rapid exchange of the coordinated CH_3CN *trans* to Cl with the deuterated solvent, only one signal due to coordinated CH_3CN at 2.60 ppm is observed, leading to the erroneous conclusion that only the *fac* isomer **1b** is present in solution. Thus, it is not clear from the published data whether samples containing only *fac*-$[RhCl_3(CH_3CH)_3]$ have actually been obtained.

X-ray structure of mer-$[RhCl_3(CH_3CN)_3]\cdot CH_3CN$ (1c). Crystals of the *mer* isomer, suitable for X-ray diffraction, were isolated during attempts to prepare $Na[RhCl_3\{HB(3,5\text{-}(CF_3)_3\text{-}pz)_3\}]$ by reacting the corresponding sodium trispyrazolylborate [10] with a mixture of **1a** and **1b**. The asymmetric unit cell contains two molecules of *mer*-$[RhCl_3(CH_3CN)_3]$ and two clathrated nitriles, these being disordered. As the two rhodium complexes in the unit cell differ only slightly in their geometry, only the structural features of one of them, i.e. that containing Rh(1), will be commented here. Fig. 3 shows an ORTEP view of *mer*-$[RhCl_3(CH_3CN)_3]$ (**1c**). A selection of bond lengths and angles is given in Table 3.

The coordination at rhodium is octahedral with minor deviations from ideal geometry. The nitriles are coordinated through the nitrogen atoms, adopting the *mer* configuration, as do the chlorides. The Rh–Cl distances (Rh–Cl(1), 2.335(2); Rh–Cl(3), 2.339(2); Rh–Cl(2), 2.289(2) Å) are not unusual [27–29]. The latter separation may reflect the higher *trans* influence of chloride relative to that of the nitrile nitrogens, even though these differences are only three standard deviations.

Interestingly, in the structurally characterized examples of complexes of the type $[Rh(III)Cl_3L_3]$ with nitrogen donors, i.e. those where L = pyridine [27] and benzothiazole-*N* [28], and L_3 = bis(oxazolinylpyridine) [29], the *trans* influence of the chloride is much less pronounced than in **1ca**.

The Rh–N distances in **1c** (Rh–N(1), 1.979(6); Rh–N(3), 1.969(7); Rh–N(2), 2.009(8) Å) are in good agreement with those reported in the above compounds [27–29]. Also these separations show the differences in bond lengths, expected on the basis of *trans* influence considerations, although these here are even less than three standard deviations. Distances and angles within the acetonitrile ligands also correspond to those found in the few reported in complexes containing coordinated CH_3CN [30–33]. The Rh(1)–N(3)–C(5) fragments are almost linear, the largest deviation being 174.4°.

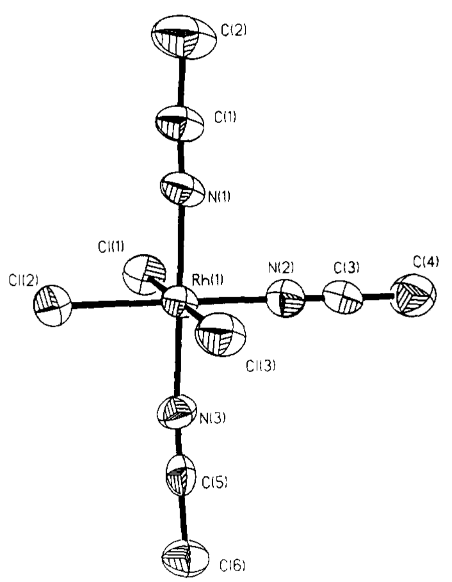


Fig. 3. ORTEP view of *mer*-$[RhCl_3(CH_3CN)_3]$ as present in *mer*-$[RhCl_3(CH_3CN)_3]\cdot CH_3CN$ (**1c**) with the atom numbering scheme (the clathrated acetonitrile molecule is not shown).

Table 3
Bond lengths (Å) and angles (°) for **1c**

Rh(1)–Cl(1)	2.339(2)	Rh(1)–N(1)	1.979(6)
Rh(1)–Cl(2)	2.289(3)	Rh(1)–N(2)	2.009(8)
Rh(1)–Cl(3)	2.335(2)	Rh(1)–N(3)	1.969(7)
N(1)–C(1)	1.131(10)	C(1)–C(2)	1.435(12)
N(2)–C(3)	1.143(12)	C(3)–C(4)	1.445(14)
N(3)–C(5)	1.135(10)	C(5)–C(6)	1.470(10)
Cl(1)–Rh(1)–Cl(2)	89.8(1)	Cl(1)–Rh(1)–Cl(3)	179.5(1)
Cl(2)–Rh(1)–Cl(3)	90.6(1)	Cl(1)–Rh(1)–N(1)	89.7(1)
Cl(2)–Rh(1)–N(1)	89.3(2)	Cl(3)–Rh(1)–N(1)	90.6(1)
Cl(1)–Rh(1)–N(2)	89.7(1)	Cl(2)–Rh(1)–N(2)	179.5(1)
Cl(3)–Rh(1)–N(2)	89.9(1)	N(1)–Rh(1)–N(2)	90.8(3)
Cl(1)–Rh(1)–N(3)	91.8(1)	Cl(2)–Rh(1)–N(3)	90.6(2)
Cl(3)–Rh(1)–N(3)	87.9(1)	N(1)–Rh(1)–N(3)	178.5(2)
N(2)–Rh(1)–N(3)	89.3(3)	Rh(1)–N(3)–C(5)	174.4(6)
Rh(1)–N(1)–C(1)	175.7(7)	Rh(1)–N(2)–C(3)	177.2(5)
N(1)–C(1)–C(2)	174.6(10)	N(2)–C(3)–C(4)	179.6(5)
N(3)–C(5)–C(6)	176.7(5)		

The crystal packing of **1c** shows several intermolecular contacts shorter than 3 Å. These interactions can be attributed to the formation of C–H···Cl hydrogen bonds [34,35]. Hydrogen bonding here occurs between the methyl hydrogens of both the clathrated and coordinated acetonitrile and the chlorides, linking the complexes either directly or via a clathrated acetonitrile. The observed C–H···Cl separations are between 2.66 and 2.86 Å and thus within the typical range (stronger interactions < 2.75 Å, weaker interactions 2.75 Å < C–H···Cl < 2.95 Å [35]).

4. Conclusions

The experiments described above show that the reaction of $RhCl_3 \cdot 3H_2O$ with CH_3CN normally yields mixtures of *mer-* and *fac-*$[RhCl_3(CH_3CN)_3]$ (**1a** and **1b**, respectively). These are best characterized by high-field ^1H NMR spectroscopy. These data show that the 60 MHz instrument used by Catsikis and Good [8] does not allow differentiation between the resonances of acetonitriles *trans* to chloride in **1a** and **1b**. It is also shown that the exchange rates of nitriles in *trans* positions to chlorides are faster than those in *trans* positions to another nitrile.

The published work and the experiments described above indicate that the isomeric forms or mixtures, obtained by different groups, may at least partially dependent on the actual nature of the species present in commercial '$RhCl_3 \cdot 3H_2O$'. As it is being increasingly recognized, this product contains several complexes and, therefore, given known differences in kinetic parameters, e.g. H_2O in *trans* position to Cl or another H_2O, one may expect also different rates for the formation of CH_3CN complexes from the aquo species.

5. Supplementary material

Tables of structure determination summary, anisotropic displacement coefficients (S1), H-atom coordinates and isotropic displacement coefficients (S2), and an extended list of bond distances and angles (S3) may be obtained from the authors upon request.

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