

# Preparation and Characterization of *fac*-[Rh(tacn)Cl<sub>3</sub>], *fac*-[Rh(tacn)(H<sub>2</sub>O)<sub>3</sub>](CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub>, [Rh(tacn)<sub>2</sub>]Br<sub>3</sub>·2.8H<sub>2</sub>O and *fac*-[Co(tacn)(H<sub>2</sub>O)<sub>3</sub>](CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub>·H<sub>2</sub>O. The Acid Dissociation Constants of *fac*-[M(tacn)(H<sub>2</sub>O)<sub>3</sub>]<sup>3+</sup> (M = Cr<sup>III</sup>, Co<sup>III</sup>, Rh<sup>III</sup> and Ir<sup>III</sup>; tacn = 1,4,7-triazacyclononane)

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Procedures for the preparation and isolation of *fac*-[Co(tacn)(H<sub>2</sub>O)<sub>3</sub>](CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub>·H<sub>2</sub>O and *fac*-[Rh(tacn)(H<sub>2</sub>O)<sub>3</sub>](CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub> are given together with preparations of [Rh(tacn)<sub>2</sub>]Br<sub>3</sub>·2.8H<sub>2</sub>O, *fac*-[Rh(tacn)Cl<sub>3</sub>] and *fac*-[Co(tacn)(NO<sub>2</sub>)<sub>3</sub>]. The complexes are characterized by NMR and UV/VIS spectroscopy. The concentration acid constants of *fac*-[Co(tacn)(H<sub>2</sub>O)<sub>3</sub>]<sup>3+</sup> and *fac*-[Rh(tacn)(H<sub>2</sub>O)<sub>3</sub>]<sup>3+</sup> were determined, and the thermodynamic parameters are compared with those of the corresponding chromium(III) and iridium(III) compounds.

In the past 20 years numerous papers concerning complexes of 1,4,7-triazacyclononane (tacn) have been published (Ref. 1 and references therein). However, only a few papers have dealt with the isolation of monomeric triqua tacn compounds.<sup>2,3</sup> Recently the synthesis and the concentration acid dissociation constants of *fac*-[Ir(tacn)(H<sub>2</sub>O)<sub>3</sub>]<sup>3+</sup> were published.<sup>2</sup> This complex was prepared by aquation of<sup>4</sup> *fac*-[Ir(tacn)Cl<sub>3</sub>] in the presence of silver ions assisted by mercury(II) in 1 M CF<sub>3</sub>SO<sub>3</sub>H. The triqua complex was easily isolated as the trifluoromethanesulfonate (triflate) salt by reducing the volume of the solution.

In the present paper we report the preparation and the acid dissociation constants of *fac*-[Co(tacn)(H<sub>2</sub>O)<sub>3</sub>](CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub>·H<sub>2</sub>O and *fac*-[Rh(tacn)(H<sub>2</sub>O)<sub>3</sub>](CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub>. The pK<sub>a</sub>-values are compared with those of the corresponding chromium(III) and iridium(III) complexes. The syntheses of *fac*-[Co(tacn)(NO<sub>2</sub>)<sub>3</sub>], *fac*-[Rh(tacn)Cl<sub>3</sub>] and [Rh(tacn)<sub>2</sub>]Br<sub>3</sub>·2.8H<sub>2</sub>O from the hydrochloride of the amine are also given.

## Experimental

**Materials.** 1,4,7-Triazacyclononane trihydrochloride (tacn·3HCl) and solutions of AgCF<sub>3</sub>SO<sub>3</sub> and Hg(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub> in CF<sub>3</sub>SO<sub>3</sub>H were prepared according to the literature.<sup>2,5</sup> All other chemicals were of analytical or reagent grade and were used without further purification.

**Instrumentation.** Absorption spectra were recorded on a Perkin–Elmer Lambda 17 spectrophotometer. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a modified (250 MHz) Bruker HX-270 spectrometer in D<sub>2</sub>O with dioxane as internal reference. The chemical shifts, δ, are given in ppm relative to TMS. The [H<sup>+</sup>] measurements were carried out using a Radiometer PHM52 digital pH-meter equipped with a G202C glass electrode and a K401 calomel electrode also from Radiometer. In the latter electrode the initial saturated potassium chloride solution was replaced with 1.0 M sodium chloride solution.

**Analyses.** C, H, N and Cl analyses were performed by the Microanalytical Laboratory at the H. C. Ørsted Institute, Copenhagen.

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*Synthetic procedures*

*fac*-[Co(*tacn*)(NO<sub>2</sub>)<sub>3</sub>]. A solution of 1.00 g of *tacn*·3HCl (4.19 mmol) and 0.54 g of LiOH·H<sub>2</sub>O (12.9 mmol) in 10 ml of water was added to a solution of 1.70 g of Na<sub>3</sub>[Co(NO<sub>2</sub>)<sub>6</sub>] (4.21 mmol) in 6 ml of water. A copious precipitate formed immediately. The mixture was heated in boiling water for 0.5 h and then cooled in ice. The precipitate was filtered off, washed, first with 2 × 10 ml of water, then twice with 96% ethanol, and finally twice with diethyl ether, and dried in air. Yield: 1.1 g (80%) of yellow *fac*-[Co(*tacn*)(NO<sub>2</sub>)<sub>3</sub>]. (Found: C 22.28; H 4.70; N 25.85. Calc. for CoC<sub>6</sub>H<sub>15</sub>N<sub>6</sub>O<sub>6</sub>: C 22,10; H 4.64; N 25.77).

*fac*-[Co(*tacn*)(H<sub>2</sub>O)<sub>3</sub>](CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub>·H<sub>2</sub>O. To 1.00 g of *fac*-[Co(*tacn*)(NO<sub>2</sub>)<sub>3</sub>] (3.07 mmol) was added 5 ml of 7.7 M CF<sub>3</sub>SO<sub>3</sub>H. The mixture was heated in boiling water for 0.5 h during which red-violet crystals precipitated. After cooling in ice the crystals were filtered off, washed three times with diethyl ether, and dried in air. Yield: 1.7 g (78%) of violet *fac*-[Co(*tacn*)(H<sub>2</sub>O)<sub>3</sub>](CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub>·H<sub>2</sub>O. (Found: C 15.27; H 3.17; N 5.92. Calc. for CoC<sub>9</sub>H<sub>23</sub>N<sub>3</sub>F<sub>9</sub>S<sub>3</sub>O<sub>13</sub>: C 15.28; H 3.28; N 5.94). <sup>1</sup>H NMR (D<sub>2</sub>O) δ 2.62–2.68 (6H, m, -CH<sub>2</sub>-) and δ 3.05–3.13 (6H, m, -CH<sub>2</sub>-). <sup>13</sup>C (D<sub>2</sub>O) δ 53.70 (6C, s, -CH<sub>2</sub>-).

*fac*-[Rh(*tacn*)Cl<sub>3</sub>]. A solution of 0.975 g of *tacn*·3HCl (4.09 mmol) in 15 ml of water was added dropwise with stirring to a solution of 1.00 g of RhCl<sub>3</sub>·3H<sub>2</sub>O (3.80 mmol) in 10 ml of water during a period of 10 min. After the addition of ca. 1 ml a precipitate started to form. As the mixture, during a period of ca. 8 min, was heated to boiling the precipitate dissolved, and just before the boiling point the yellow product started to precipitate. Finally the mixture was boiled for 5 min, to yield a yellow precipitate in an orange solution with pH ca. 0.5. After standing for 2 h the precipitate was filtered off, washed, first with 3 × 5 ml of water, then with 96% ethanol and finally with diethyl ether, and dried in air. Yield: 1.22 g (95%) of yellow *fac*-[Rh(*tacn*)Cl<sub>3</sub>]. (Found: C 20.57; H 4.54; N 12.17; Cl 31.00. Calc. for RhC<sub>6</sub>H<sub>15</sub>N<sub>3</sub>Cl<sub>3</sub>: C 21.29; H 4.47; N 12.42; Cl 31.42).

*fac*-[Rh(*tacn*)(H<sub>2</sub>O)<sub>3</sub>](CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub>. To 1.21 g of *fac*-[Rh(*tacn*)Cl<sub>3</sub>] (3.57 mmol) was added 11.8 ml of a 1.0 M solution of AgCF<sub>3</sub>SO<sub>3</sub> in 3.5 M CF<sub>3</sub>SO<sub>3</sub>H and 0.2 ml of a 0.50 M solution of Hg(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub> in 3.5 M CF<sub>3</sub>SO<sub>3</sub>H and the mixture was boiled until the yellow precipitate had dissolved. The mixture was then heated to 80 °C for 3 h before the AgCl was filtered off and washed with water until the filtrate was colourless. The filtrate and washings were evaporated as much as possible on a rotating vacuum evaporator (final bath temp. 50 °C) and the solution was then left overnight at 5 °C for crystallization. The crystals were filtered off, washed thoroughly with diethyl ether and dried in air. Yield: 2.4 g (92%) of light yellow *fac*-[Rh(*tacn*)(H<sub>2</sub>O)<sub>3</sub>](CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub>. (Found: C 14.68; H 2.89; N 5.72. Calc. for RhC<sub>9</sub>H<sub>21</sub>N<sub>3</sub>F<sub>9</sub>S<sub>3</sub>O<sub>12</sub>: C

14.74; H 2.89; N 5.73). <sup>1</sup>H NMR (D<sub>2</sub>O) δ 2.88–2.97 (6H, m, -CH<sub>2</sub>-) and δ 3.10–3.21 (6H, m, -CH<sub>2</sub>-). <sup>13</sup>C (D<sub>2</sub>O) δ 53.91 (6C, s, -CH<sub>2</sub>-).

[Rh(*tacn*)<sub>2</sub>]Br<sub>3</sub>·2.8H<sub>2</sub>O. To a suspension of 0.85 g of *fac*-[Rh(*tacn*)Cl<sub>3</sub>] (2.5 mmol) in 70 ml of water was added one half of a solution of 1.10 g of *tacn*·3HCl (4.61 mmol) and 0.58 g of LiOH·H<sub>2</sub>O (14 mmol) in 10 ml of water. The mixture was refluxed for 10 min, after which the other half of the *tacn* solution was added and the reflux continued for 1 h. The solution was then left in an oven at 130 °C overnight, and the yellow residue was then extracted with 96% ethanol and filtered. The remanence was extracted on the filter with, in all, 50 ml of water, the filtrate was evaporated to dryness, and the residue was washed, first with 96% ethanol and then diethyl ether and dried in air. The crude [Rh(*tacn*)<sub>2</sub>]Cl<sub>3</sub>·aq (ca. 1.3 g) was dissolved in 10 ml of boiling water and the solution was filtered. 1.0 g of NaBr·2H<sub>2</sub>O (7.2 mmol) was dissolved in the filtrate by heating to boiling, and the solution was left for crystallization. The mixture was cooled in ice before the crystals were filtered off and washed, first with 1 ml of ice-cold water, then three times with 96% ethanol and finally with diethyl ether, and dried in air. Yield: 1.1 g (67%) of white [Rh(*tacn*)<sub>2</sub>]Br<sub>3</sub>·2.8H<sub>2</sub>O. (Found: C 22.23; H 5.94; N 12.92; Br 36.58. Calc. for RhC<sub>12</sub>H<sub>35.6</sub>N<sub>6</sub>Br<sub>3</sub>O<sub>2.8</sub>: C 22.12; H 5.51; N 12.90; Br 36.80). <sup>1</sup>H NMR (D<sub>2</sub>O) δ 2.90–2.99 (12H, m, -CH<sub>2</sub>-) and δ 3.13–3.20 (12H, m, -CH<sub>2</sub>-). <sup>13</sup>C (D<sub>2</sub>O) δ 53.13 (12C, s, -CH<sub>2</sub>-).

*Determination of acid dissociation constants.* The concentration acid dissociation constants of *fac*-[M(*tacn*)(H<sub>2</sub>O)<sub>3</sub>]<sup>3+</sup> (M = chromium(III), cobalt(III) and rhodium(III)) were determined by regression analysis of the titration data as described by Mønsted and Mønsted.<sup>6</sup> The determinations were made at 25 ± 0.1 and 40 ± 0.1 °C in 1 M NaClO<sub>4</sub>. ΔH° and ΔS° were calculated from these results assuming temperature independence in this interval, and the standard deviations are referring to 1σ. The results are given in Table 1.

**Results and discussion**

*Syntheses.* The complex *fac*-[Rh(*tacn*)(H<sub>2</sub>O)<sub>3</sub>]<sup>3+</sup> has been prepared by aquation of *fac*-[Rh(*tacn*)Cl<sub>3</sub>] in the presence of silver ions assisted by mercury(II) in 3.5 M CF<sub>3</sub>SO<sub>3</sub>H. Omission of Hg<sup>II</sup> leads to substitution of less than three of the chloride ions. A similar observation was also made in the preparation<sup>2</sup> of *fac*-[Ir(*tacn*)(H<sub>2</sub>O)<sub>3</sub>]<sup>3+</sup>. Triflate has been shown to be a useful counter-ion for the isolation of the monomeric *tacn* triqua complexes of the group nine members Co<sup>III</sup>, Rh<sup>III</sup> and Ir<sup>III</sup>, as the compounds *fac*-[M(*tacn*)(H<sub>2</sub>O)<sub>3</sub>](CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub> are easily isolated by evaporation of their reaction mixtures and removing the remaining CF<sub>3</sub>SO<sub>3</sub>H by washing with diethyl ether. The hydrochloride of the amine has been used in this work, since this is more easily obtained than the free amine. In

Table 1. Thermodynamic parameters for the consecutive acid dissociation constants of *fac*-[M(tacn)(H<sub>2</sub>O)<sub>3</sub>]<sup>3+</sup> in 1.0 M NaClO<sub>4</sub> at 25.0°C.<sup>a</sup> (M=Cr<sup>III</sup>, Co<sup>III</sup>, Rh<sup>III</sup> and Ir<sup>III</sup>).

Metal	Constant	Value	$\Delta H^\circ /$ kJ mol <sup>-1</sup>	$\Delta S^\circ /$ J mol <sup>-1</sup> K <sup>-1</sup>
Cr <sup>III</sup> <sup>b</sup>	pK <sub>a1</sub>	4.538(8)	36.5(17)	35(6)
	pK <sub>a2</sub>	6.784(8)	38.7(17)	0(6)
	pK <sub>a3</sub>	8.883(10)	38.3(21)	-42(7)
Co <sup>III</sup> <sup>b</sup>	pK <sub>a1</sub>	5.658(5)	43.4(9)	37(3)
	pK <sub>a2</sub>	7.788(8)	46.0(14)	5(5)
	pK <sub>a3</sub>	9.657(11)	37.4(19)	-59(7)
Rh <sup>III</sup> <sup>b</sup>	pK <sub>a1</sub>	6.114(10)	42.1(13)	24(4)
	pK <sub>a2</sub>	7.924(17)	38.0(22)	-24(8)
	pK <sub>a3</sub>	9.600(21)	36.9(28)	-60(9)
Ir <sup>III</sup> <sup>c</sup>	pK <sub>a1</sub>	5.912(10)	36.6(17)	10(6)
	pK <sub>a2</sub>	7.658(14)	39.1(24)	-16(8)
	pK <sub>a3</sub>	9.319(17)	37.2(30)	-54(10)

<sup>a</sup> The standard deviations are given in parentheses; i.e. 36.6(17) means 36.6 ± 1.7. <sup>b</sup> This work. <sup>c</sup> From Ref. 2.

addition to this, the yields of the rhodium(III) compounds are higher than published earlier<sup>7</sup> using the free amine.

**NMR spectra and electronic spectra.** All the <sup>1</sup>H NMR spectra show two groups of multiplet resonances due to methylene protons. The magnetic inequivalence observed for coordinated tacn is expected, and originates from the different orientations of the two groups of protons toward the metal ion center, which has been discussed earlier.<sup>2,8</sup>

The absorption spectra of *fac*-[Co(tacn)(H<sub>2</sub>O)<sub>3</sub>]<sup>3+</sup> and of *fac*-[Rh(tacn)(H<sub>2</sub>O)<sub>3</sub>]<sup>3+</sup> are shown in Fig. 1. Both spectra show two bands, which are assigned as the two spin-allowed transitions <sup>1</sup>A<sub>1</sub> → <sup>1</sup>A<sub>2</sub>, <sup>1</sup>E(C<sub>3v</sub>) and

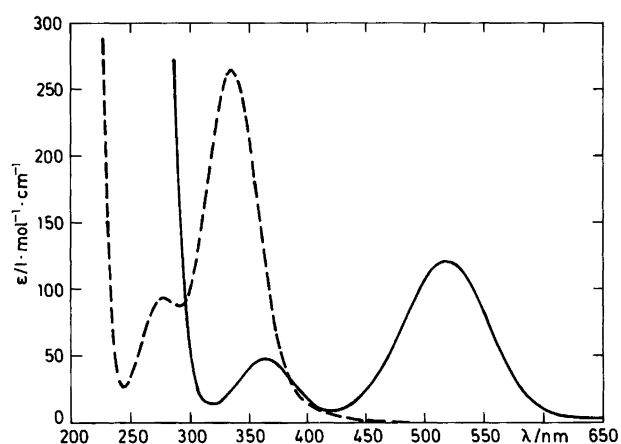


Fig. 1. Absorption spectra of *fac*-[Co(tacn)(H<sub>2</sub>O)<sub>3</sub>](CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub>·H<sub>2</sub>O (full line) and of *fac*-[Rh(tacn)(H<sub>2</sub>O)<sub>3</sub>](CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub> (dotted line) both dissolved in 1.0 M CF<sub>3</sub>SO<sub>3</sub>H. The extrema are [λ/nm(ε/l mol<sup>-1</sup> cm<sup>-1</sup>)]: For Co: 519(121); 420(8.4); 363(47.5); 318(13) and for Rh: 335(265); 291(87); 277(93); 244(26).

<sup>1</sup>A<sub>1</sub> → <sup>1</sup>A<sub>1</sub>, <sup>1</sup>E(C<sub>3v</sub>), respectively. The lack of splitting is explainable by the holohedric symmetry being approximately O<sub>h</sub>. The energy of the first d-d band of the two triaqua complexes is close to the average value of the energies of the first d-d bands in [M(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup> [Co<sup>III</sup> = 1.65 μm<sup>-1</sup> (Ref. 9); Rh<sup>III</sup> = 2.52 μm<sup>-1</sup> (Ref. 10)] and in [M(tacn)<sub>2</sub>]<sup>3+</sup>, [Co<sup>III</sup> = 2.18 μm<sup>-1</sup> (Ref. 11); Rh<sup>III</sup> = 3.40 μm<sup>-1</sup>], respectively. This result is in accordance with the transferability of angular overlap model parameters,<sup>12,13</sup> and similar results have also been observed<sup>2</sup> for the analogous iridium(III) complex and in a series<sup>14</sup> of facial triamines of chromium(III).

The maxima in the spectrum of [Rh(tacn)<sub>2</sub>]<sup>3+</sup> (Fig. 2) are (with respect to wavelength) in agreement with the values published by Wiegardt *et al.*<sup>7</sup> [λ<sub>max</sub>(ε<sub>max</sub>) = 294(265) and 249(216)], whereas we find lower values for the molar absorptivities. However, the elemental analysis performed by Wiegardt *et al.* indicates five molecules of water of crystallization, whereas ours indicates 2.8H<sub>2</sub>O/Rh in two individual preparations. If we assume 5H<sub>2</sub>O/Rh, we get the same ε-values as Wiegardt *et al.* Gaussian analysis and ligand field analysis of the spectrum of [Rh(tacn)<sub>2</sub>]<sup>3+</sup> and of a series of other ammine and amine complexes of cobalt(III), rhodium(III) and iridium(III) have been published.<sup>10</sup>

**Acid-base properties.** The thermodynamic parameters of the acid dissociation constants of coordinated water ligands in *fac*-[M(tacn)(H<sub>2</sub>O)<sub>3</sub>]<sup>3+</sup> [M = chromium(III), cobalt(III), rhodium(III) and iridium(III)] are shown in Table 1. The order of decreasing acidity of the complexes is Cr<sup>III</sup> > Co<sup>III</sup> > Ir<sup>III</sup> > Rh<sup>III</sup>, which is similar to the order observed for the *cis*-diaqua complexes of these metal ions, containing ammonia<sup>15</sup> or ethylenediamine.<sup>16</sup> The difference between the first two pK<sub>a</sub>-values, ΔpK<sub>a</sub> = pK<sub>a2</sub> - pK<sub>a1</sub>, is 2.25, 2.13, 1.81 and 1.75 for Cr<sup>III</sup>, Co<sup>III</sup>, Rh<sup>III</sup> and Ir<sup>III</sup>, respectively. These magnitudes and order of the ΔpK<sub>a</sub>-values are also observed for the abovementioned *cis*-diaqua complexes, and indicate the *cis*-config-

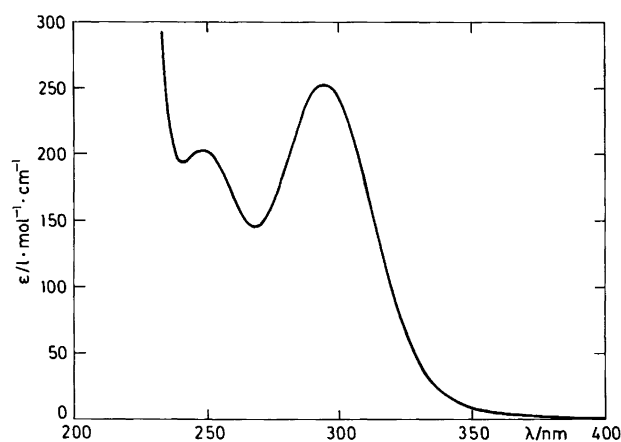


Fig. 2. Absorption spectrum of [Rh(tacn)<sub>2</sub>]<sub>3</sub>Br<sub>3</sub>·2.8H<sub>2</sub>O dissolved in water. The extrema are [λ/nm(ε/l mol<sup>-1</sup> cm<sup>-1</sup>)]: 295(253); 268(145); 249(203); 241(192).

uration of coordinated water, since the *trans*-configuration has a much larger  $\Delta pK_a$  of ca. 3.6–2.9 units, due to the tendency of a lower  $pK_{a1}$ -value of the *trans*-configuration.<sup>15,16</sup> The variation of the values of  $\Delta H^\circ$  and  $\Delta S^\circ$  for a given *fac*-[M(tacn)(H<sub>2</sub>O)<sub>3</sub>]<sup>3+</sup> complex ion shows that  $\Delta H^\circ$  is almost constant while  $\Delta S^\circ$  displays a significant decrease from positive to negative values which causes a decrease in the consecutive  $K_a$ -values. A similar trend has been observed for the *cis*- and *trans*-diaqua complexes of iridium(III) with ammonia and ethylenediamine.<sup>17</sup>

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