

# Preparation, Isolation and Characterization of *fac*-[Ir(tacn)(H<sub>2</sub>O)<sub>3</sub>](CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub>, *fac*-[Ir(tacn)(CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub>] and [Ir(tacn)<sub>2</sub>]Cl<sub>3</sub>·<sup>1</sup>/<sub>2</sub>HCl·4H<sub>2</sub>O. Crystal Structure of [Ir(tacn)<sub>2</sub>]Cl<sub>3</sub>·<sup>1</sup>/<sub>2</sub>HCl·4H<sub>2</sub>O (tacn = 1,4,7-Triazacyclononane)

Claus Flensburg, Kim Simonsen\* and Lars Kobberøe Skov

Department of Chemistry, H.C. Ørsted Institute, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen Ø, Denmark

Flensburg, C., Simonsen, K. and Skov, L. K., 1994. Preparation, Isolation and Characterization of *fac*-[Ir(tacn)(H<sub>2</sub>O)<sub>3</sub>](CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub>, *fac*-[Ir(tacn)(CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub>] and [Ir(tacn)<sub>2</sub>]Cl<sub>3</sub>·<sup>1</sup>/<sub>2</sub>HCl·4H<sub>2</sub>O. Crystal Structure of [Ir(tacn)<sub>2</sub>]Cl<sub>3</sub>·<sup>1</sup>/<sub>2</sub>HCl·4H<sub>2</sub>O (tacn = 1,4,7-Triazacyclononane). – Acta Chem. Scand. 48: 209–214 © Acta Chemica Scandinavica 1994.

Procedures are given for the preparations of *fac*-[Ir(tacn)(H<sub>2</sub>O)<sub>3</sub>](CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub>, *fac*-[Ir(tacn)(CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub>] and [Ir(tacn)<sub>2</sub>]Cl<sub>3</sub>·<sup>1</sup>/<sub>2</sub>HCl·4H<sub>2</sub>O (tacn = 1,4,7-triazacyclononane). The concentration acidity constants of *fac*-[Ir(tacn)(H<sub>2</sub>O)<sub>3</sub>]<sup>3+</sup> were determined (25°C, 1.0 M NaClO<sub>4</sub>), [pK<sub>a1</sub> = 5.912(10), pK<sub>a2</sub> = 7.658(14) and pK<sub>a3</sub> = 9.319(17)]. The crystal structure of [Ir(tacn)<sub>2</sub>]Cl<sub>3</sub>·<sup>1</sup>/<sub>2</sub>HCl·4H<sub>2</sub>O was determined by single-crystal X-ray diffraction (Trigonal, R32, hexagonal axes, *a* = 8.043(2), *c* = 31.821(9) Å, *Z* = 3).

The past three decades have seen an increasing interest in compounds of macrocyclic poly-aza ligands such as 1,4,7-triazacyclononane (tacn), which are known to form thermodynamically stable and kinetically inert complexes. The ligand tacn has been coordinated to most of the first-row transition metals, several of the second- and third-row transition metals and main-group metals; their chemistry has been thoroughly investigated by several authors and notably described by Wieghardt *et al.* (Ref. 1 and references therein).

In contrast to publications on other metals, the number of papers concerning macrocyclic amine complexes of iridium(III) is rather limited; one reason for this may originate in problems in preparative chemistry.

The kinetic inertia of iridium(III) compounds is, in addition to their tendency toward reduction to iridium metal, a complicating feature in their preparative chemistry. The syntheses of a(m)mine complexes<sup>2–5</sup> of iridium(III) require rather harsh conditions, i.e. high temperatures and prolonged reaction times. However, for reactions with cyclic amines this causes a problem, since cyclic amines tend to reduce IrCl<sub>3</sub>·aq to metal at elevated temperatures. In the preparation of iridium(III) complexes with the saturated macrocyclic amines 1,4,8,11-tetraazacyclotetradecane<sup>6</sup> (cyclam) and 1,4,7-triazacyclononane<sup>7</sup> (tacn), the use of starting compounds other than IrCl<sub>3</sub>·aq and K<sub>2</sub>IrCl<sub>6</sub> has been introduced.

In the present paper, which is a continuation of the synthesis and crystal structure determination of *fac*-[Ir(tacn)Cl<sub>3</sub>] published earlier,<sup>7</sup> we report the preparation, isolation and characterization of *fac*-[Ir(tacn)(H<sub>2</sub>O)<sub>3</sub>](CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub>, *fac*-[Ir(tacn)(CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub>] and [Ir(tacn)<sub>2</sub>]Cl<sub>3</sub>·<sup>1</sup>/<sub>2</sub>HCl·4H<sub>2</sub>O, and the crystal structure of [Ir(tacn)<sub>2</sub>]Cl<sub>3</sub>·<sup>1</sup>/<sub>2</sub>HCl·4H<sub>2</sub>O.

## Experimental

**Materials.** The preparation of *fac*-[Ir(tacn)Cl<sub>3</sub>] has been described previously.<sup>7</sup> 1,4,7-Triazacyclononane trihydrochloride (tacn·3HCl) and Ag<sub>2</sub>CO<sub>3</sub> were prepared according to the literature.<sup>8,9</sup> Stock solution A, containing 1.00 M AgCF<sub>3</sub>SO<sub>3</sub> in 3.5 M CF<sub>3</sub>SO<sub>3</sub>H, was made by dissolving 13.79 g of Ag<sub>2</sub>CO<sub>3</sub> (50.0 mmol) in 100 ml of 4.5 M CF<sub>3</sub>SO<sub>3</sub>H, and stock solution B, containing 0.50 M 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, was made by dissolving 10.83 g of HgO (50.0 mmol) in 100 ml of 4.5 M CF<sub>3</sub>SO<sub>3</sub>H. 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 Bruker MSL-300 spectrometer in D<sub>2</sub>O or DMSO-d<sub>6</sub> with TMS as external reference, and chemical shifts, δ, are given in ppm relative to this standard. Single-crystal data were

\* To whom correspondence should be addressed.

collected with an Enraf-Nonius CAD4 diffractometer. The  $[H^+]$  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, Cl and S analyses were performed by the Micro-analytic Laboratory at the H.C. Ørsted Institute, Copenhagen.

#### Synthetic procedures

*fac-[Ir(tacn)(H<sub>2</sub>O)<sub>3</sub>](CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub>.* 1.00 g of *fac*-[Ir(tacn)Cl<sub>3</sub>] (2.34 mmol) was added to a solution consisting of 7.0 ml of stock solution A, 0.5 ml of stock solution B and 17.5 ml water. The suspension was refluxed for 8 h, during which time silver chloride precipitated and a golden orange solution was formed. The mixture was then cooled in ice, and the silver chloride was filtered off and washed with 2 × 5 ml of ice-cold water. To the filtrate and washings were added 6 ml of 8 M CF<sub>3</sub>SO<sub>3</sub>H, and the solution was placed for evaporation in a desiccator over P<sub>4</sub>O<sub>10</sub>, whereby long white crystals were formed. The crystals were filtered off and washed with 2 × 4 ml of 8 M CF<sub>3</sub>SO<sub>3</sub>H, then thoroughly with diethyl ether and dried in air. Yield: 1.3 g (68%) of white *fac*-[Ir(tacn)(H<sub>2</sub>O)<sub>3</sub>](CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub>. Further evaporation of the filtrate and CF<sub>3</sub>SO<sub>3</sub>H washings yields a second crop of *fac*-[Ir(tacn)(H<sub>2</sub>O)<sub>3</sub>](CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub>. Yield: 0.3 g (15%). (Found: C 13.03; H 2.63; N 5.07; S 11.8. Calc. for IrC<sub>9</sub>H<sub>21</sub>N<sub>3</sub>F<sub>9</sub>S<sub>3</sub>O<sub>12</sub>: C 13.14; H 2.57; N 5.11; S 11.69). <sup>1</sup>H NMR (DMSO-d<sub>6</sub>) δ = 2.73–2.79 (6H, m, -CH<sub>2</sub>-), δ = 2.88–2.92 (6H, m, -CH<sub>2</sub>-), δ = 7.62 (3H, b, -NH) and δ = 8.04 (6H, b, -OH<sub>2</sub>). <sup>13</sup>C NMR (DMSO-d<sub>6</sub>) δ = 53.75 (6C, s, -CH<sub>2</sub>-).

*fac-[Ir(tacn)(CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub>].* To 2.00 g of *fac*-[Ir(tacn)(H<sub>2</sub>O)<sub>3</sub>](CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub> (3.43 mmol) were added 4 ml of neat trifluoromethanesulfonic acid, and the suspension was heated at 120–125 °C for 3 h with stirring and under a gentle stream of nitrogen. During the reaction time a yellow solution was formed, and pale yellow crystals precipitated. The mixture was then cooled in ice, and the crystals were filtered off, washed with diethyl ether and dried in air. Yield: 1.7 g (91%) of pale yellow *fac*-[Ir(tacn)(CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub>]. (Found: C 13.97; H 1.92; N 5.45; S 13. Calc. for IrC<sub>9</sub>H<sub>15</sub>N<sub>3</sub>F<sub>9</sub>S<sub>3</sub>O<sub>9</sub>: C 14.04; H 1.97; N 5.47; S 12.51).

*[Ir(tacn)<sub>2</sub>]Cl<sub>3</sub>·1/2HCl·4H<sub>2</sub>O.* 1.00 g of *fac*-[Ir(tacn)Cl<sub>3</sub>] (2.34 mmol) was placed in a teflon container, and a solution of 1.00 g of tacn·3HCl·H<sub>2</sub>O (3.90 mmol) and 0.49 g of LiOH·H<sub>2</sub>O (11.7 mmol) in 20 ml of water was added. The container was closed and placed in an autoclave containing water for pressure equilibration. The

Table 1. Thermodynamic parameters for *fac*-[Ir(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>

Constant	Value	ΔH°/KJmol <sup>-1</sup>	ΔS°/Jmol <sup>-1</sup> K <sup>-1</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) ≡ 36.6 ± 1.7.

autoclave was closed and heated at 170 °C for 72 h and subsequently allowed to cool to room temperature with the oven. The resulting orange solution was filtered and evaporated to dryness on a rotating vacuum evaporator. The remanence was extracted with portions of 96% ethanol until the filtrate became colourless (ca. 50 ml). The light-yellow residue was dissolved in 3 ml of boiling water, the solution was filtered and 3 ml of 4 M HCl were added to the filtrate. The solution was left for crystallization overnight. The crystals were filtered off, washed with 2 × 2 ml of 4 M HCl, then with 2 × 2 ml of 96% ethanol and dried in air. Yield: 0.15 g (10%) of white [Ir(tacn)<sub>2</sub>]Cl<sub>3</sub>·1/2HCl·4H<sub>2</sub>O.\* (Found: C 21.80; H 5.99; N 12.86; Cl 19.45. Calc. for IrC<sub>12</sub>H<sub>38.5</sub>N<sub>6</sub>Cl<sub>3.5</sub>O<sub>4</sub>: C 22.06; H 6.87; N 12.86; Cl 18.99). <sup>1</sup>H NMR (D<sub>2</sub>O) δ = 2.92–2.98 (12H, m, -CH<sub>2</sub>-) and δ = 3.11–3.17 (12H, m, -CH<sub>2</sub>-). <sup>13</sup>C NMR (D<sub>2</sub>O) δ = 52.25 (12C, s, -CH<sub>2</sub>-).

*Determination of acid dissociation constants.* The concentration acid dissociation constants of *fac*-[Ir(tacn)(H<sub>2</sub>O)<sub>3</sub>]<sup>3+</sup> were determined by regression analysis of the titration data as described by Mønsted and Mønsted.<sup>10</sup> The determinations were made at 25 and 40 °C in 1 M NaClO<sub>4</sub>. The results are given in Table 1.

*Crystal structure determination of [Ir(tacn)<sub>2</sub>]Cl<sub>3</sub>·1/2HCl·4H<sub>2</sub>O.* Diffraction data were collected for a tabular colourless crystal with dimensions 0.19 × 0.22 × 0.19 mm. Three reflections were measured every 2.8 h to check for crystal decay. A linear decrease was observed during the data collection period to a total of 4.5%. 4925 individual reflections were measured. The diffraction symmetry was 3 *m* and from the observed systematic absences the space group was determined to be *R*32. Crystal data and details about the structure determination are listed in Table 2. The data reduction performed with the DREADD<sup>11</sup> programs included corrections for decay, Lorentz effects, polarization effects and absorption. The Gaussian integration method was employed for the latter correction using the program ABSORB.<sup>12</sup> Symmetry-related reflections were averaged, giving 829 unique reflections (*R*<sub>int</sub> = 0.069). The structure was solved using SHELXS-86<sup>13</sup> and refined with SHELXL-93.<sup>14</sup> Atomic scattering factors were taken from Refs. 15 and 16. The least-squares refinement in-

\* The content of HCl of crystallization found by titration analyses varied between 0.4 and 0.7 per Ir.

Table 2. Crystallographic data for  $[\text{Ir}(\text{tactn})_2]\text{Cl}_3 \cdot \frac{1}{2}\text{HCl} \cdot 4\text{H}_2\text{O}$ .

Formula	$\text{C}_{12}\text{H}_{38.5}\text{N}_6\text{Cl}_{3.5}\text{O}_4\text{Ir}$
Formula weight/g mol <sup>-1</sup>	647.26
Space group	Trigonal, $R\bar{3}2$ (No. 155)
Temperature/K	122 (1)
Hexagonal axes:	
$a/\text{Å}$	8.043 (2)
$c/\text{Å}$	31.821 (9)
$V/\text{Å}^3$	1783 (1)
$Z$	3
$D_c/\text{g cm}^{-3}$	1.809
Radiation $\lambda$ (CuK $\alpha$ )/Å	1.541 80
Abs. coeff. $\mu/\text{cm}^{-1}$	146.5
Absorption: numerical	$T_{\text{min}}=0.086$ , $T_{\text{max}}=0.246$
Max $2\theta/^\circ$	149
Total no. of reflections	4925
No. of unique data ( $I > 2\sigma(I)$ )	829
$R$	0.017
$R_{w2}$	0.046

cluded atomic coordinates and anisotropic thermal parameters for all non-hydrogen atoms, and an extinction parameter, to a total of 60 parameters.  $\Sigma w(F_o^2 - F_c^2)^2$  was minimized,  $w^{-1} = \sigma^2(F_o^2) + (0.0326P)^2 + 4.198P$  and  $P = (F_o^2 + 2F_c^2)/3$ . The sites of Cl2 and O2 were only partly occupied, 75 and 50%, respectively. After the final refinement cycle the agreement factors were  $R = 0.017$  ( $R = \Sigma |F_o - F_c| / \Sigma F_o$ ) for 829  $F_o > 4\sigma(F_o)$ ,  $R_{w2} = 0.046$  ( $R_{w2} = [\Sigma \{w(F_o^2 - F_c^2)\}^2 / \Sigma \{wF_o^2\}^2]^{1/2}$ ) and  $S = 1.164$ , and the maximum shift was  $0.001\sigma$ . The absolute structure parameter,<sup>17</sup>  $\eta$ , was  $-0.04(3)$ . The final difference synthesis had the highest and lowest values of 0.82 and  $-0.49 \text{ e Å}^{-3}$ , respectively; as expected located around Ir. Atomic coordinates and thermal parameters are listed in Table 3, and bond lengths and angles are listed in Tables 4 and 5. Figures 1 and 2 are ORTEP<sup>18</sup> drawings of the complex and the unit cell. Tables of anisotropic thermal parameters and a listing of observed and calculated structure factors are available from the authors on request.

Table 3. Final positional and thermal parameters (in Å<sup>2</sup>).<sup>a</sup>

Atom	$x/a$	$y/b$	$z/c$	$U_{\text{eq}}/U_{\text{iso}}$
Ir	0.0000	0.0000	0.0000	0.01494 (13)
N	-0.1108 (13)	0.1154 (12)	-0.04303 (7)	0.0209 (5)
C1	0.0573 (8)	0.2885 (7)	-0.0617 (2)	0.0247 (10)
C2	-0.2348 (7)	-0.0310 (7)	-0.0754 (2)	0.0237 (10)
Cl1	-0.3333	0.3333	-0.01844 (4)	0.0285 (2)
Cl2	0.3333	0.6667	-0.14396 (7)	0.0434 (4)
O1	-0.0394 (10)	0.3333	-0.1667	0.079 (2)
O2	-0.3333	0.3333	-0.2015 (5)	0.067 (3)
H1	-0.17 (2)	0.17 (2)	-0.0338 (11)	0.027*
H2	0.025 (12)	0.330 (13)	-0.082 (3)	0.032*
H3	0.104 (8)	0.378 (8)	-0.041 (2)	0.032*
H4	-0.349 (11)	-0.005 (11)	-0.078 (2)	0.031*
H5	-0.156 (8)	0.005 (7)	-0.097 (2)	0.031*

<sup>a</sup>Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter, defined as:

$$U_{\text{eq}} = 1/3 \Sigma U_{ij} a_i^* a_j^* a_i \cdot a_j$$

$U_{\text{iso}}$  for the starred atoms were calculated as  $1/3 U_{\text{eq}}$  for the corresponding heavy atom.

Table 4. Interatomic distances (in Å).<sup>a</sup>

Ir	N	2.087 (2)
N	C1	1.496 (10)
N	C2	1.506 (8)
N	H1	0.84 (4)
C1	C2 <sup>ii</sup>	1.508 (5)
C1	H2	0.82 (9)
C1	H3	0.90 (6)
C2	H4	1.04 (7)
C2	H5	0.87 (5)

<sup>a</sup>Symmetry operation: <sup>ii</sup>  $-x+y, -x, z$ .

Table 5. Bond angles (in °).<sup>a</sup>

N	Ir	N <sup>ii</sup>	81.64 (10)
N	Ir	N <sup>i</sup>	97.7 (3)
N	Ir	N <sup>v</sup>	99.0 (4)
N	Ir	N <sup>iii</sup>	179.0 (5)
C1	N	C2	113.2 (4)
C1	N	Ir	106.6 (4)
C2	N	Ir	111.4 (4)
N	C1	C2 <sup>ii</sup>	108.7 (4)
N	C2	C1 <sup>iv</sup>	111.2 (4)

<sup>a</sup>Symmetry operations: <sup>i</sup>  $-x, -x+y, -z$ ; <sup>ii</sup>  $-x+y, -x, z$ ; <sup>iii</sup>  $y, x, -z$ ; <sup>iv</sup>  $-y, x-y, z$ ; <sup>v</sup>  $x-y, -y, -z$ .

## Results and discussion

**Syntheses.** The complex *fac*- $[\text{Ir}(\text{tactn})(\text{H}_2\text{O})_3]^{3+}$  has been prepared by aqation of *fac*- $[\text{Ir}(\text{tactn})\text{Cl}_3]$  in the presence of silver ions assisted by mercury(II) in 1 M  $\text{CF}_3\text{SO}_3\text{H}$ . Omission of Hg(II) leads to substitution of less than three of the chloride ions. A similar observation was made in the reaction of *fac*- $[\text{Ir}(\text{tactn})\text{Cl}_3]$  with neat trifluoromethanesulfonic acid, triflic acid, which only lead to replacement of two of the chloride ligands by triflate ions. This was in contrast to earlier experimental observations in which all the chloride ions in *cis*- or *fac*-isomers could be substituted with triflate ions.<sup>19</sup> The reason for this is unknown, however. Steric hindrance between three fa-

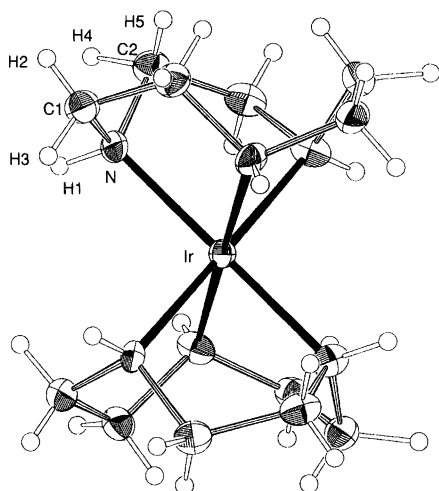


Fig. 1. ORTEP drawing of  $[\text{Ir}(\text{tacn})_2]^{3+}$ .

cially coordinated  $\text{CF}_3\text{SO}_3^-$  ions is not the cause, since reaction of  $\text{fac-}[\text{Ir}(\text{tacn})(\text{H}_2\text{O})_3](\text{CF}_3\text{SO}_3)_3$  with neat triflic acid easily and in high yield forms  $\text{fac-}[\text{Ir}(\text{tacn})(\text{CF}_3\text{SO}_3)_3]$ .

The complex  $\text{fac-}[\text{Ir}(\text{tacn})(\text{CF}_3\text{SO}_3)_3]$  was believed to be useful for further syntheses; however, owing to insolubility in common solvents and even in boiling acidic solution, reactions with this compound have so far been unsuccessful.

The bis(tacn)iridium(III) compound was prepared from reaction of  $\text{fac-}[\text{Ir}(\text{tacn})\text{Cl}_3]$  and an excess of  $\text{tacn}\cdot 3\text{HCl}$  in aqueous  $\text{LiOH}$  solution at elevated temperature. No sign of deposited metal was observed; however, the yield of  $[\text{Ir}(\text{tacn})_2]^{3+}$  was rather low. On

crystallization from  $\text{HCl}$  solution spontaneous resolution of the racemate occurs, as a crystal contains only one enantiomer. An aqueous solution of these crystals was acidic, and titration analyses found between 0.4 and 0.7 mol strong acid per mol of complex.

**Structure.** For both  $\text{fac-}[\text{Ir}(\text{tacn})(\text{H}_2\text{O})_3](\text{CF}_3\text{SO}_3)_3$  and  $[\text{Ir}(\text{tacn})_2]\text{Cl}_3\cdot\frac{1}{2}\text{HCl}\cdot 4\text{H}_2\text{O}$  crystals suitable for single-crystal X-ray diffraction could be obtained, while this was not the case for  $\text{fac-}[\text{Ir}(\text{tacn})(\text{CF}_3\text{SO}_3)_3]$ . Unfortunately, we have not been able to interpret the diffraction pattern of  $\text{fac-}[\text{Ir}(\text{tacn})(\text{H}_2\text{O})_3](\text{CF}_3\text{SO}_3)_3$  in a way that is consistent with the presumed molecular symmetry.<sup>20</sup> For  $[\text{Ir}(\text{tacn})_2]\text{Cl}_3\cdot\frac{1}{2}\text{HCl}\cdot 4\text{H}_2\text{O}$  the crystal structure determination established the identity of this complex. It crystallizes with iridium at the special position (0,0,0) with the site symmetry 32. The structure is depicted in Fig. 1, showing the iridium complex and the labelling of the atoms, and in Fig. 2 illustrating the crystal packing. In Fig. 3 the hydrogen bonding between the amine protons and chloride ions is shown [ $\text{N}\cdots\text{Cl1} = 3.166(3) \text{ \AA}$ ]. Bond lengths and angles of the complex are given in Tables 4 and 5. The overall structure is very similar to those of  $[\text{Co}\{(\text{R})\text{-Metacn}\}_2]_3\cdot 5\text{H}_2\text{O}$ ,<sup>21</sup>  $[\text{Fe}(\text{tacn})_2]\text{Cl}_3\cdot 5\text{H}_2\text{O}$ <sup>22</sup> and probably also  $[\text{Co}(\text{tacn})_2]\text{Cl}_3\cdot 5\text{H}_2\text{O}$ .<sup>23</sup> In contrast to these structures, we find an excess of chloride ions and less oxygen corresponding to water molecules. To maintain electroneutrality  $\text{H}_3\text{O}^+$  must be found on some water sites. The structure (Fig. 2) consists of alternating layers of (a)  $[\text{Ir}(\text{tacn})_2]^{3+}$  ions and chloride ions (Cl1) and (b) water molecules (O1 and O2) and chloride ions (Cl2). In the latter layer some of the positions are only partially occupied (Cl2 75% and O2 50%). There is extensive hydrogen bonding within the layers, but only van der Waals

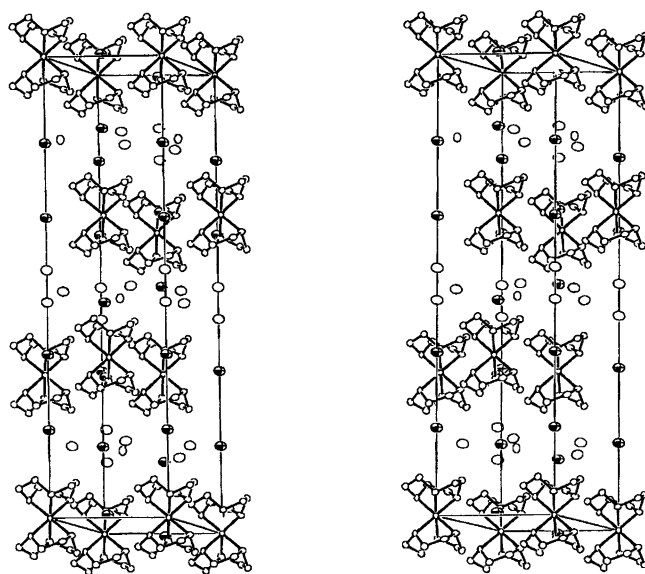


Fig. 2. Stereoscopic ORTEP drawing of the unit cell of  $[\text{Ir}(\text{tacn})_2]\text{Cl}_3\cdot\frac{1}{2}\text{HCl}\cdot 4\text{H}_2\text{O}$ . The shaded ellipsoids represent chloride ions.

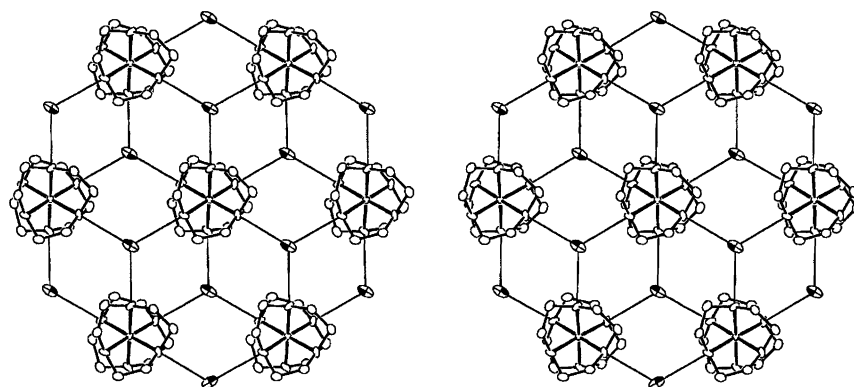


Fig. 3. View down the three-fold axis of the layer of the complex cations illustrating the hydrogen-bonding pattern between amine protons and chloride ions [ $N \cdots Cl$  3.166(3) Å].

interactions between the layers. The Ir–Ir distance of neighbouring complex ions is 8.04 Å, while the Ir–Ir distance between complexes in adjacent layers is 11.6 Å. The bond lengths and angles of the tactn ligands in this complex are very similar to those of other transition-metal tactn complexes.<sup>1</sup> The conformation of each five-membered Ir–N–C–C–N–Ir ring is  $\lambda$ , and hence the complex is optically active (the space group  $R32$  is optically active). The Ir–N bond lengths [2.087(2) Å] are slightly longer than found in  $[\text{Ir}(\text{tactn})\text{Cl}_3]$  (average 2.06 Å).<sup>7</sup> The coordination geometry around the iridium atom is trigonal-distorted octahedral, with small *cis* N–Ir–N (within one tactn ligand) angles at 81.7° and large *cis* N–Ir–N (between two tactn ligands) angles at 97.7 and 99.0°, while the *trans* N–Ir–N angle is 179.0°. This rather large deviation is probably caused by steric constraints of the nine-membered macrocyclic ring.

**NMR spectra.** The  $^1\text{H}$  spectra of  $[\text{Ir}(\text{tactn})_2]^{3+}$  as well as  $\text{fac-}[\text{Ir}(\text{tactn})(\text{H}_2\text{O})_3]^{3+}$  show two groups of multiplet resonances in the region of methylene protons. The observed magnetic inequivalence of the methylene protons arises from the different positions of the two groups of protons in the coordinated tactn ligand, i.e. equatorial and axial positions with respect to the nitrogen plane, which cause different orientations toward the iridium(III) centre. The two different kinds of methylene protons (H2,H5 and H3,H4) are seen in Fig. 1. A similar spectrum has also been observed for the corresponding  $[\text{Co}(\text{tactn})_2]^{3+}$  complex.<sup>24</sup>

**Spectral properties.** The absorption spectra of  $[\text{Ir}(\text{tactn})_2]^{3+}$  and  $\text{fac-}[\text{Ir}(\text{tactn})(\text{H}_2\text{O})_3]^{3+}$  are shown in Figs. 4 and 5. The spectrum of  $[\text{Ir}(\text{tactn})_2]^{3+}$  shows two transition at 242 and 222 nm, which are assigned as two singlet transitions corresponding to  $^1A_{1g} \rightarrow ^1T_{1g}$  and  $^1A_{1g} \rightarrow ^1T_{2g}$ , respectively, in strict octahedral symmetry. The position of the second observed d-d band seems to support the assignment<sup>5</sup> of the shoulder at 226 nm in the spectrum of  $[\text{Ir}(\text{NH}_3)_6]^{3+}$  as the transition  $^1A_{1g} \rightarrow ^1T_{2g}$ .

The spectrum of  $\text{fac-}[\text{Ir}(\text{tactn})(\text{H}_2\text{O})_3]^{3+}$  shows three transitions at 275, 238 and 204 nm. The band at 275 nm and the shoulder at 238 nm are assigned as the two spin-allowed transitions  $^1A_1 \rightarrow ^1A_2, ^1E$  and  $^1A_1 \rightarrow ^1A_1, ^1E$ , respectively. The lack of splitting is explainable by the holohedric symmetry being approximately  $O_h$ . It is to be noticed that the energy of the first d-d band at 275 nm ( $3.64 \mu\text{m}^{-1}$ ) is close to the average value of the energies of the first d-d bands in  $[\text{Ir}(\text{tactn})_2]^{3+}$  (242 nm;  $4.13 \mu\text{m}^{-1}$ ) and in  $[\text{Ir}(\text{H}_2\text{O})_6]^{3+}$  (314 nm;  $3.18 \mu\text{m}^{-1}$ ).<sup>7</sup> As pointed out by Yamatera<sup>25</sup> and Schäffer and Jørgensen,<sup>26</sup> this is the expected result if angular overlap model parameter transferability is assumed. The origin of the shoulder at 204 nm is unknown; a similar ‘third band’ has also been observed<sup>5</sup> in the spectra of  $[\text{Ir}(\text{NH}_3)_6]^{3+}$  and  $[\text{Ir}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+}$  and is believed not to be of d-d nature.

**Acid properties.** The concentration acid dissociation constants of  $\text{fac-}[\text{Ir}(\text{tactn})(\text{H}_2\text{O})_3]^{3+}$  (Table 1) show a difference between the consecutive  $\text{p}K_a$ -values at ca. 1.7 units. This order of separation has also been observed for *cis-*

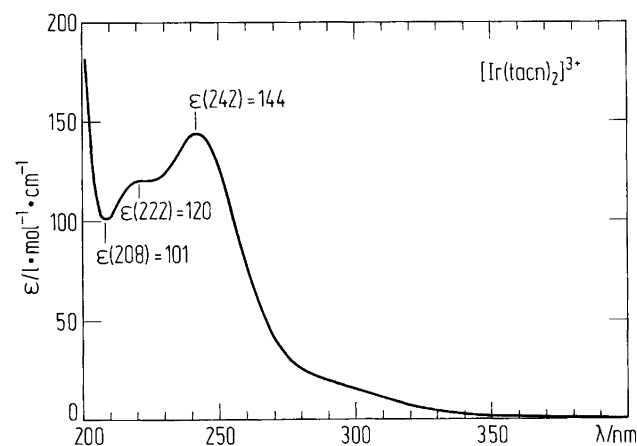


Fig. 4. Absorption spectrum of  $[\text{Ir}(\text{tactn})_2]^{3+}$  in  $\text{H}_2\text{O}$ .

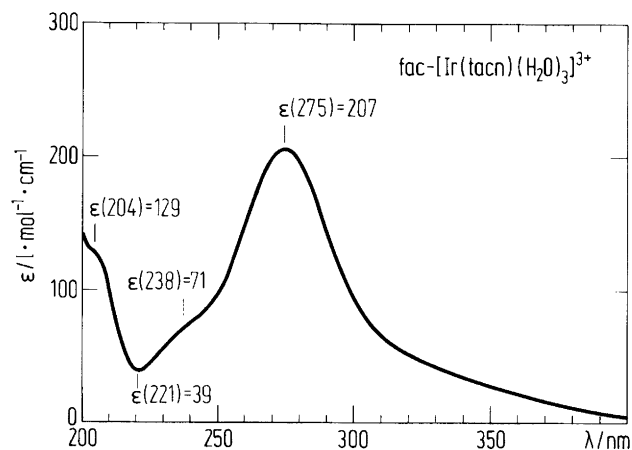


Fig. 5. Absorption spectrum of  $fac-[Ir(tacn)(H_2O)_3]^{3+}$  in 1.0 M  $HClO_4$ .

diaquairidium(III) complexes containing ammonia<sup>27</sup> or ethylenediamine<sup>28</sup> and indicates a *cis*-configuration of the coordinated water, since a *trans*-configuration has a much larger separation of ca. 3 units.<sup>27,28</sup> The  $pK_a$ -values of  $fac-[Cr(tacn)(H_2O)_3]^{3+}$  are reported<sup>29</sup> to be 4.44(2), 6.60(1) and 8.72(1), respectively, showing the higher acidity of chromium(III) complexes compared to analogous iridium(III) complexes.<sup>27,28</sup>

### Conclusions

The compounds described in this paper were all prepared from  $fac-[Ir(tacn)Cl_3]$ . Coordinated chloride in  $fac-[Ir(tacn)Cl_3]$  could be substituted with water by reaction of silver ions in a synthesis that seems to be catalyzed by mercury(II). The structural assignments were made from their NMR spectra, electronic spectra and acid dissociation constants.  $[Ir(tacn)_2]^{3+}$  was found to resolve spontaneously when crystallized as  $[Ir(tacn)_2]Cl_3 \cdot \frac{1}{2}HCl \cdot 4H_2O$ .

**Acknowledgement.** We thank Mr. Flemming Hansen for technical assistance with the crystallographic work and Drs. Peter Andersen, Frode Galsbøl and Sine Larsen for valuable discussions and suggestions. Financial support by the Danish Natural Science Research Council through grants nos. 11-8096 and 11-8128 is gratefully acknowledged.

### References

1. Chaudhuri, P. and Wieghardt, K. *Progr. Inorg. Chem.* 35 (1987) 329.
2. Galsbøl, F. *Acta Chem. Scand., Ser. A32* (1978) 757.
3. Galsbøl, F. and Rasmussen, B. S. *Acta Chem. Scand., Ser. A36* (1982) 83.
4. Galsbøl, F. and Rasmussen, B. S. *Acta Chem. Scand., Ser. A36* (1982) 439.
5. Galsbøl, F., Hansen, S. K. and Simonsen, K. *Acta Chem. Scand.* 44 (1990) 796.
6. Mønsted, L., Mønsted, O., Nord, G. and Simonsen, K. *Acta Chem. Scand.* 47 (1993) 439.
7. Gajhede, M., Simonsen, K. and Skov, L. K. *Acta Chem. Scand.* 47 (1993) 271.
8. Searle, G. H. and Geue, R. J. *Aust. J. Chem.* 37 (1984) 959.
9. Palmer, W. G. In: *Experimental Inorganic Chemistry*, The University Press, Cambridge 1962, p. 150.
10. Mønsted, L. and Mønsted, O. *Acta Chem. Scand., Ser. A30* (1976) 203.
11. Blessing, R. H. *Crystallogr. Rev.* 1 (1987) 3.
12. DeTitta, G. T. *J. Appl. Crystallogr.* 18 (1985) 75.
13. Sheldrick, G. M. In: Sheldrick, G. M., Kruger, C. and Goddard, R., Eds., *Crystallographic Computing*, Oxford University Press, Oxford 1985, Vol. 3, p. 175.
14. Sheldrick, G. M. *J. Appl. Crystallogr.* To be published.
15. Cromer, D. T. and Waber, J. T. In: *International Tables for X-ray Crystallography*. The Kynoch Press, Birmingham 1974, Vol. IV, Table 2.2B.
16. Wilson, A. J. C. In: *International Tables for X-ray Crystallography*, Kluwer Academic Publishers, Dordrecht, The Netherlands 1992, Vol. C, Tables 6.1.1.3, 4.2.6.8 and 4.2.4.2.
17. Flack, H. D. *Acta Crystallogr., Sect. A39* (1983) 876.
18. Johnson, C. K. ORTEPII Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN 1970.
19. Dixon, N. E., Lawrance, G. A., Lay, P. A., Sargeson, A. M. and Taube, H. *Inorg. Synth.* 24 (1986) 289.
20. Flensburg, C., Larsen, S., Simonsen, K. and Skov, L. K. *Unpublished results*.
21. Mikami, M., Kuroda, R. and Saito, Y. *Acta Crystallogr., Sect. B33* (1977) 1485.
22. Boeyens, J. C. A., Forbes, A. G. S., Hancock, R. D. and Wieghardt, K. *Inorg. Chem.* 24 (1985) 2926.
23. Dubicki, L., Ferguson, J., Geue, R. J. and Sargeson, A. M. *Chem. Phys. Lett.* 74 (1980) 393.
24. Küppers, H.-J., Neves, A., Pomp, C., Ventur, D., Wieghardt, K., Nuber, B. and Weiss, J. *Inorg. Chem.* (1986) 2400.
25. Yamatera, H. *Bull. Chem. Soc. Jpn.* 31 (1958) 95.
26. Schäffer, C. E. and Jørgensen, C. K. *Dan. Vidensk. Selsk., Mat.-Fys. Medd.* 34 (1965) No. 13.
27. Galsbøl, F., Simonsen, K. and Springborg, J. *Acta Chem. Scand.* 465 (1992) 915.
28. Galsbøl, F. and Rasmussen, B. S. *Acta Chem. Scand., Ser. A38* (1984) 141.
29. Døssing, A., Ph.D. Thesis, University of Copenhagen (1990).

Received September 1, 1993.