

The Preparation and Crystal Structure of *fac*-[Ir(tacn)Cl₃] (tacn = 1,4,7-triazacyclononane) and the Preparation of Cs[Ir(H₂O)₆](SO₄)₂ · 6H₂O

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A procedure is given for the preparation of *fac*-[Ir(tacn)Cl₃] (tacn = 1,4,7-triazacyclononane) from the iridium(III) alum, and a straightforward method for synthesis of Cs[Ir(H₂O)₆](SO₄)₂ · 6H₂O in good yield is also given. The crystal structure of *fac*-[Ir(tacn)Cl₃] was determined by single-crystal X-ray diffraction (orthorhombic, *P*na21, *a* = 12.0487(15), *b* = 7.969(2), *c* = 10.9735(11) Å, *Z* = 4).

In the past decade numerous papers concerning 1,4,7-triazacyclononane (tacn) complexes have been published (Ref. 1 and references therein). In particular, complexes of the transition metals have been thoroughly investigated by Wieghardt *et al.*^{2–4} However, even though several rhodium(III) complexes containing tacn are fully described,⁴ none has to our knowledge been reported for iridium(III). Neither has a crystal structure of an uncharged *fac*-[M(tacn)Cl₃] complex (M = metal) been reported.

In the present paper we report the preparation and the crystal structure determination of *fac*-[Ir(tacn)Cl₃]. Attempts to prepare *fac*-[Ir(tacn)Cl₃] by the methods used for the preparations of 1,2-ethanediamineiridium(III) complexes⁵ or of the ammineiridium(III) complexes⁶ did not lead to the desired product. In the search for a starting material other than IrCl₃ · aq or K₂IrCl₆ we have tried the hexaaquairidium(III) complex, which was first prepared by Gamsjäger.^{7,8} This species proved successful for reaction with tacn · 3HCl in acidic solution. We therefore also give a straightforward method for the synthesis of Cs[Ir(H₂O)₆](SO₄)₂ · 6H₂O in good yield.

Experimental

Materials. 1,4,7-triazacyclononane trihydrochloride (tacn · 3HCl) was prepared according to the literature.⁹ All other chemicals were of analytical or reagent grade and were used without further purification.

Instrumentation. The absorption spectrum was recorded on a Perkin-Elmer Lambda 17 spectrophotometer and the solid-state ¹³C NMR spectrum was recorded on a Bruker MSL-300 NMR spectrometer.

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

Synthetic procedures.

Cs[Ir(H₂O)₆](SO₄)₂ · 6H₂O. 5.00 g of K₂IrCl₆ (10.35 mmol) were added to 3 l of 0.1 M NaOH and the mixture was stirred at ca. 30°C for 6 h, during which the colour of the solution changed from deep red–brown to greenish and finally to yellow. The solution was then placed at 5°C overnight. 1.0 g of ascorbic acid was added to the now light-blue solution and pH was adjusted to 7 with 6 M HClO₄, during which the colour of the solution turned yellow and iridium(III) hydroxide precipitated. The mixture was then allowed to stand at 5°C for a few hours in order to complete sedimentation. Most of the solution was removed by decantation and the solid was isolated by centrifugation. The 'Ir(OH)₃' was dissolved in 10 ml of 2 M H₂SO₄, a small amount of iridium metal was removed from the solution by filtration through a 0.45 μm pore size filter, and a filtered solution of 12 g of Cs₂SO₄ (34 mmol) in 10 ml of water was added. The solution was allowed to stand for crystallization, first at room temperature for some hours and then at 5°C overnight. The crystals were filtered off, washed with 2 × 5 ml of ice-cold water and dried in air. Yield: 4.5–5.0 g (59–66%) of yellow Cs[Ir(H₂O)₆](SO₄)₂ · 6H₂O.

fac-[Ir(tacn)Cl₃]. 3.00 g of Cs[Ir(H₂O)₆](SO₄)₂ · 6H₂O (4.09 mmol) were added to a filtered solution of 3.15 g of tacn · 3HCl · H₂O (12.3 mmol) and 6.0 g of Cs₂SO₄ (17 mmol) in 30 ml of water. The mixture was heated to boiling for complete dissolution and the solution was then heated without stirring at 95°C for 48 h. During the reaction, crystals precipitated. The mixture was allowed to cool slowly to room temperature and the crystals were filtered off, washed with water and dried in air. Yield: 1.1 g

Table 1. Crystallographic data.

Formula	$C_6H_{15}N_3Cl_3Ir$
Formula weight/g mol ⁻¹	427.77
Space group	Orthorhombic, <i>Pna</i> 21 (No. 33)
Temperature/K	122
<i>a</i> /Å	12.0487(15)
<i>b</i> /Å	7.969(2)
<i>c</i> /Å	10.9735(11)
<i>V</i> /Å ³	1053.7
<i>Z</i>	4
Radiation, λ (MoK α)/Å	0.71069
Abs. coeff., μ /cm ⁻¹	133.53
Max 2 θ /°	51
Total no. of reflections	6360
No. of unique data [<i>I</i> > 3 σ (<i>I</i>)]	3800
<i>R</i>	0.026
<i>R</i> _w	0.031

(63%) of yellow *fac*-[Ir(tacn)Cl₃]. (Found: C 16.76; H 3.56; N 9.75; Cl 23.76. Calc. for IrC₆H₁₅N₃Cl₃: C 16.86; H 3.53; N 9.82; Cl 24.86).

Solid-state ¹³C NMR. The ¹³C NMR spectrum of the solid sample was recorded at 75.468 MHz with the cross-polarization/magic angle spinning (CP/MAS) technique; a spectral width of 29412 Hz and an accumulation of 1400 transients with an acquisition time of 0.14 s were used. The spectrometer was calibrated relative to TMS using an external sample, and side-bands were suppressed by the TOSS sequence. The spectrum showed two broad signals at 53.0 and 57.7 ppm. The signal at 57.7 ppm had a slightly higher intensity than that at 53.0 ppm. The presence of two signals was supported by looking at the derivative spectrum.

Crystal structure determination of *fac*-[Ir(tacn)Cl₃]. A summary of the crystallographic data is given in Table 1.

Table 2. Final positional and displacement parameters (in Å²) for non-hydrogen atoms.^a

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i> _{eq}
Ir	0.06845(1)	0.06710(2)	-0.036	0.642(1)
Cl1	0.0425(1)	0.2689(2)	-0.1905(1)	1.20(2)
Cl2	0.0520(1)	0.2795(2)	0.1176(1)	1.10(2)
Cl3	-0.12702(9)	0.0196(2)	-0.0190(2)	1.40(2)
N1	0.0969(5)	-0.1309(6)	-0.1525(5)	1.16(6)
N2	0.1046(4)	-0.1085(6)	0.0966(5)	1.19(6)
N3	0.2377(3)	0.0884(4)	-0.0447(4)	0.80(5)
C1	0.0613(5)	-0.2859(7)	-0.0821(6)	1.34(8)
C2	0.1163(5)	-0.2834(6)	0.0423(6)	1.25(7)
C3	0.2124(5)	-0.0535(7)	0.1557(6)	1.28(7)
C4	0.2948(5)	-0.0084(8)	0.0567(6)	1.43(8)
C5	0.2707(5)	0.0285(8)	-0.1669(6)	1.41(8)
C6	0.2125(5)	-0.1363(8)	-0.1921(6)	1.33(8)

^a Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter, defined as:

$$B_{eq} = \frac{1}{3} [a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + 2abc \cos(\gamma) \beta_{12} + 2accos(\beta) \beta_{13} + 2bccos(\alpha) \beta_{23}]$$

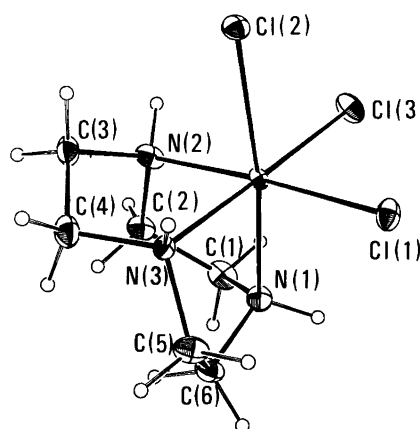
Fig. 1. ORTEP drawing of *fac*-[Ir(tacn)Cl₃].

Table 3. Interatomic distances (in Å).

Ir-Cl1	2.362(1)	N2-C2	1.523(7)
Ir-Cl2	2.393(1)	N2-C3	1.516(8)
Ir-Cl3	2.392(1)	N3-C4	1.520(8)
Ir-N1	2.061(5)	N3-C5	1.478(8)
Ir-N2	2.063(5)	C1-C2	1.519(9)
Ir-N3	2.048(4)	C3-C4	1.515(9)
N1-C1	1.519(8)	C5-C6	1.515(9)
N1-C6	1.460(8)		

Table 4. Bond Angles (in °).

Cl1-Ir-Cl2	90.79(5)	Ir-N1-C1	105.1(4)
Cl1-Ir-Cl3	91.86(5)	Ir-N1-C6	111.5(4)
Cl2-Ir-Cl3	88.70(5)	C1-N1-C6	113.4(5)
Cl1-Ir-N1	95.4(1)	Ir-N2-C2	111.4(4)
Cl1-Ir-N2	175.4(2)	Ir-N2-C3	106.6(3)
Cl1-Ir-N3	92.4(1)	C2-N2-C3	110.6(4)
Cl2-Ir-N1	172.6(1)	Ir-N3-C4	111.9(3)
Cl2-Ir-N2	90.1(1)	Ir-N3-C5	106.6(3)
Cl2-Ir-N3	93.4(1)	C4-N3-C5	112.3(4)
Cl3-Ir-N1	95.1(2)	N1-C1-C2	108.9(5)
Cl3-Ir-N2	92.7(2)	N2-C2-C1	108.9(4)
Cl3-Ir-N3	175.4(1)	N2-C3-C4	108.9(5)
N1-Ir-N2	83.3(2)	N3-C4-C3	110.5(5)
N1-Ir-N3	82.4(2)	N3-C5-C6	108.8(5)
N2-Ir-N3	83.1(2)	N1-C6-C5	111.2(5)

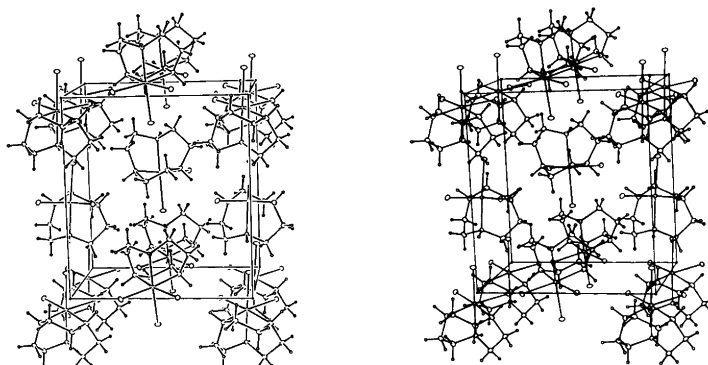


Fig. 2. Stereoscopic ORTEP drawing of the unit cell of *fac*-[Ir(tacn)Cl₃].

Diffraction data were collected on a tabular yellow crystal with dimensions $0.16 \times 0.14 \times 0.28$ mm with an Enraf-Nonius CAD4 diffractometer. Three reflections were measured every 2.8 h to check for crystal decay, and there was found a 7% linear decrease during the data collection period. A total of 6360 individual reflections were measured and reduced, including corrections for decay, Lorentz effects, polarization effects and absorption, to values of $|F_o|$ and $\sigma(F_o)$ for 6359 unique reflections. 3800 reflections for which $I > 3\sigma(I)$ were included in the final structure analysis. The structure was solved using SHELXS-86,¹⁰ and refined with the SDP package.¹¹ Atomic scattering factors were taken from Ref. 12, except for hydrogen.¹³ Atomic coordinates and anisotropic thermal parameters for all non-hydrogen atoms, a total of 117 parameters, were refined minimizing $\sum w(|F_o| - |F_c|)^2$, where $w^{-1} = \sigma^2(F_o) + 0.01\sigma F_o^2$. Positions of the hydrogen atoms were calculated. After the final refinement cycle the agreement factors were $R = 0.026$, $R_w = 0.031$ and $S = 2.109$, and the maximum ratio (Δ/σ) was 0.01. A final Fourier synthesis gave the highest and lowest residuals as 3.143 and $-3.401 \text{ e } \text{\AA}^{-3}$, respectively, located around Ir sites. Atomic coordinates and thermal parameters are listed in Table 2, and bond lengths and angles are listed in Tables 3 and 4. Figs. 1 and 2 are ORTEP drawings of the complex and the unit cell. Tables of anisotropic thermal parameters, hydrogen positions and a listing of observed and calculated structure factor amplitudes are available from the authors on request.

Results and discussion

The iridium(III) alum, which has been prepared in good yield and by a straightforward synthesis without use of column chromatography, can be identified by its electronic absorption spectrum as shown in Fig. 3. This compound proved to be a useful starting material in the synthesis of *fac*-[Ir(tacn)Cl₃]. No sign of reduction of the hexaaquairidium(III) ion to iridium metal has been observed when working with the tacn ligand at pH below 3. The pH of the reaction solution was kept at ca. 2 using Cs₂SO₄ as a buffer, and thereby having about 50% of

the once-deprotonated ligand ($pK_{a1} \approx 2.1$).¹ The chloride ions necessary for the preparation of the [Ir(tacn)Cl₃] complex originates from tacn·3HCl, and one of the driving forces in this synthesis might be the precipitation of the practically insoluble inner complex during the reaction.

The crystal structure determination established the identity of the complex. To our knowledge it is the first inner complex of the type *fac*-[Ir(tacn)X₃] (X = halide ion) to be structurally characterized. Indeed, it is one of the few facial triam(m)inetrihalide complexes for which the structure has been determined. The structure is shown in Fig. 1, and bond lengths and angles of the complex are given in Tables 3 and 4. The bond lengths and angles of the tacn ligand in this complex are very similar to those of other transition-metal tacn complexes.¹ The conformations of the three five-membered Ir–N–C–C–N rings are either ($\delta\delta\delta$) or ($\lambda\lambda\lambda$). Both are present in the unit cell and are connected by a glide plane. The six carbon atoms can be divided into two groups by their C–Ir distances: group 1 (C1, C3 and C5) having an average distance of 2.87 Å, and group 2 (C2, C4 and C6) with an average distance of 2.96 Å. The Ir–N bond lengths (average 2.06 Å) and Ir–Cl bond lengths (average 2.38 Å) are very close to those found in the *mer*-[Ir(en)(en*)Cl₃] complex

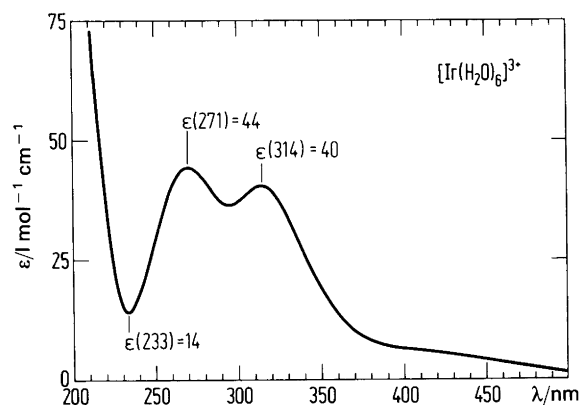


Fig. 3. Absorption spectrum of Cs[Ir(H₂O)₆](SO₄)₂·6H₂O in 1.0 M CF₃SO₃H.

(en* = monodentate 1,2-ethanediamine).¹⁴ The coordination geometry around the iridium atom is distorted octahedral with Cl–Ir–Cl angles close to 90° (average 90.5°), but with considerably smaller N–Ir–N angles (average 82.9°). This deviation is probably caused by steric constraints of the nine-membered macrocyclic ring.

The results of the solid-state ¹³C NMR spectrum, which showed two signals, may be interpreted on the basis of the two groups of carbon atoms found in the crystal structure as described above.

The first Ir(III) tacn complex has now been reported and is available for further chemistry. Substitution of the chlorides with water is being pursued, and it is our intention to try to make binuclear complexes and to compare these with corresponding complexes of other transition metals.

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