

# The Crystal Structures of *mer*-Trichloro(1,2-ethanediamine)-(2-aminoethylammonium)iridium(III) Chloride Hydrate, *mer*-[Ir(en)(enH)Cl<sub>3</sub>]Cl·H<sub>2</sub>O, and its Conjugate Base, *mer*-[Ir(en)(en\*)Cl<sub>3</sub>]

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The crystal structures of the two title compounds have been determined by X-ray diffraction methods. *mer*-[Ir(en)(enH)Cl<sub>3</sub>]Cl·H<sub>2</sub>O crystallizes in the space group *P*2<sub>1</sub>/*n*, with *a* = 11.536(2), *b* = 11.253(1), *c* = 10.200(1) Å, β = 97.21(1)° and *Z* = 4. The crystals of *mer*-[Ir(en)(en\*)Cl<sub>3</sub>] are also monoclinic, space group *P*2<sub>1</sub>/*c*, with *a* = 8.122(3), *b* = 9.904(3), *c* = 14.199(4), β = 90.97(4)° and *Z* = 4. The coordination geometry of Ir is virtually identical in the two complexes. The Ir–Cl distances involving the *trans*-dispositioned chloride ions are identical and shorter than the distance to the *cis*-chloride ion, 2.357(2) Å compared to 2.382(3) Å. The Ir–N distances involving the unidentate ligands are larger than equivalent Ir–N bonds to the chelating en groups. The complexes differ only in the conformation of the unidentate en\* and enH<sup>+</sup> groups.

Iridium(III) complexes with 1,2-ethanediamine (en) as ligand have been known for many years. The preparation of the tris(1,2-ethanediamine)iridium(III) ion was first reported by Werner and Smirnov.<sup>1</sup> More recently some of the present authors investigated the series of iridium(III) complexes containing three, two or one 1,2-ethanediamine ligands.<sup>2,3</sup> In the investigation of iridium(III) complexes with chloride and 1,2-ethanediamine ligands, it was possible to isolate a trichloroiridium(III) complex with one unidentate and one chelating 1,2-ethanediamine ligand. The complex was characterized as the meridional isomer of the [Ir(en)(enH)Cl<sub>3</sub>]<sup>+</sup> ion (where enH<sup>+</sup> denotes the 2-aminoethylammonium ion) and the corresponding deprotonated complex containing one non-protonated unidentate en ligand (en\*), *mer*-[Ir(en)(en\*)Cl<sub>3</sub>], was also isolated.

Numerous structure determinations have been performed for coordination compounds with 1,2-ethanediamine as a bidentate ligand. Many complexes which contain the 2-aminoethylammonium ion, enH<sup>+</sup>, as ligand have also been described. The first one, *fac*-[Cr(en)(enH)Cl<sub>3</sub>]Cl, was prepared by Werner.<sup>4</sup> Although some of them were even isolated in the solid state, only two Pt complexes, [Pt(enH)Cl<sub>3</sub>]·H<sub>2</sub>O and [Pt(enH)Cl<sub>3</sub>], have previously been characterized structurally.<sup>5,6</sup> In order to contribute to the

structural characteristics of complexes with the enH<sup>+</sup> ion as a ligand and also to allow a comparison between equivalent complexes with enH<sup>+</sup> and en as ligands, we have undertaken structure determinations for *mer*-[Ir(en)(enH)Cl<sub>3</sub>]Cl·H<sub>2</sub>O and *mer*-[Ir(en)(en\*)Cl<sub>3</sub>].

## Experimental

Carbon-13 NMR spectra were recorded in D<sub>2</sub>O on Bruker HX270 and JEOL JNM-FX-200 spectrometers using 1,4-dioxane as internal standard. Chemical shifts δ(positive downfield) are given in ppm relative to this standard. *mer*-[Ir(en)(enH)Cl<sub>3</sub>]Cl·H<sub>2</sub>O was synthesized as described earlier;<sup>3</sup> <sup>13</sup>C NMR (D<sub>2</sub>O, LiOH·H<sub>2</sub>O, ca. pD 11): δ –17.9, –19.3, –19.8, –25.3; (after acidification to ca. pD 2 with DCl): δ –19.2, –19.7, –23.3, –27.2. This latter spectrum of the essentially fully *N*-deuterated species in acid corresponded, within ± 0.2 ppm for individual peaks, to the spectrum of the initially non-deuterated, protonated complex dissolved in D<sub>2</sub>O, ca. pD 2.

*mer*-[Ir(en)(en\*)Cl<sub>3</sub>] was prepared as follows. *mer*-[Ir(en)(enH)Cl<sub>3</sub>]Cl·H<sub>2</sub>O (0.5 g, 1.1 mmol) was dissolved in 1.5 ml of boiling water. The solution was filtered and the filter washed with 0.5 ml of water. To the filtrate and washings was added 0.5 ml of 2 M KOH, which resulted in a precip-

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Table 1. Crystal data and summary of the structure determinations.

	<i>mer</i> -[Ir(en)(enH)Cl <sub>3</sub> ]Cl·H <sub>2</sub> O		<i>mer</i> -[Ir(en)(en*)Cl <sub>3</sub> ]
Formula	IrC <sub>4</sub> Cl <sub>4</sub> H <sub>19</sub> N <sub>4</sub> O		IrC <sub>4</sub> Cl <sub>3</sub> H <sub>16</sub> N <sub>4</sub>
Formula weight	473.24		418.76
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>		<i>P</i> 2 <sub>1</sub> / <i>c</i>
Temperature/K	296		291
Diffractometer	CAD 4		Syntex <i>P</i> 2 <sub>1</sub>
Cell parameters	Single crystal	Powder	
<i>a</i> /Å	11.536(2)	11.540(5)	8.122(3)
<i>b</i> /Å	11.253(1)	11.260(4)	9.904(3)
<i>c</i> /Å	10.200(1)	10.203(3)	14.199(4)
β/°	97.21(1)	97.23(3)	90.97(4)
<i>V</i> /Å <sup>3</sup>	1313.6(4)	1315(1)	1142(1)
Observed density/g cm <sup>-3</sup>	2.37		2.42
Calculated density/g cm <sup>-3</sup>	2.39		2.423
Molecules per cell	4		4
Radiation	MoKα (λ = 0.71073 Å)		MoKα (λ = 0.71073 Å)
Crystal size/mm <sup>3</sup>	0.12×0.06×0.08		0.08×0.14×0.14
Linear absorption coefficient/cm <sup>-1</sup>	109.28		131
Range of transmission factors	0.4435–0.5748		0.42–1.0 (relative)
Scan mode	ω–5θ/3		ω–2θ
θ/°	1–27		1–22.5
No. of unique reflections	2866		1339
No. of "observed" reflections	2231		1078
No. of variables	175		133
Weights, <i>w</i> <sup>-1</sup>	σ <sup>2</sup> ( <i>F</i> ) + 0.0002  <i>F</i>   <sup>2</sup>		σ <sup>2</sup> ( <i>F</i> )
<i>R</i> ( <i>F</i> )	0.020		0.026
<i>R</i> <sub>w</sub> ( <i>F</i> )	0.022		0.029

itate. This was dissolved by heating, and the solution was allowed to stand at room temperature for 2 h for crystallization. The orange crystals were filtered off, washed, (first with three 0.5 ml portions of ice-cold water, then with ethanol) and dried in air. Yield 0.28 g (63%). Anal. IrC<sub>4</sub>H<sub>16</sub>N<sub>4</sub>Cl<sub>3</sub>: C, H, N, Cl. <sup>13</sup>C NMR (D<sub>2</sub>O, ca. pD 10, LiOH·H<sub>2</sub>O): δ -18.1, -19.6, -20.0, -25.6; (after acidification to ca. pD 3 with CF<sub>3</sub>SO<sub>3</sub>H in D<sub>2</sub>O): δ -19.1, -19.7, -23.3, -27.0.

### X-Ray crystallography

Table 1 contains the crystal data for the two compounds and a summary of information describing the data collection and structure refinement. In the following a more detailed account will be given of the crystallographic characterization of the two Ir complexes.

[*Ir(en)(enH)Cl*]<sub>3</sub>Cl·H<sub>2</sub>O. This complex forms regularly shaped orange–red crystals. The crystal used for data collection was bound by the faces {011}, <-101>, <10-1> and <100>. Weissenberg and precession photographs showed that the crystals belong to the monoclinic system; the systematically absent reflections: *h*0*l* for *h* + *l* = 2*n* + 1 and 0*k*0 for *k* = 2*n* + 1 are only consistent with the space group *P*2<sub>1</sub>/*n*, a non-standard setting of *P*2<sub>1</sub>/*c*. The crystal density was determined by flotation in a mixture of 1,2-dibromoethane and 1,1,2,2-tetrabromoethane.

Diffraction data were collected at room temperature on an Enraf-Nonius CAD4 diffractometer using MoKα radiation monochromatized from a highly mosaic graphite crystal. The unit-cell dimensions were determined from a least-squares refinement of the setting angles for 25 reflections with 11.9 < θ < 23.4°. These values were in good agreement with those obtained from the Guinier powder diffraction pattern measured with CuKα radiation and using Si as the internal standard.

The scan type and scan range were selected based on a careful analysis of reflection profiles. The intensities of three standard reflections were measured after every 10<sup>4</sup> s. These measurements showed no significant variations. The orientation of the crystal was checked after every 300 reflections. Data processing included corrections for Lorentz, polarization and absorption effects; the latter correction was performed using the Gaussian numerical integration procedure.<sup>7</sup> The symmetry-related reflections were averaged, resulting in 2866 independent reflections. The 2231 of these which had *I*/σ(*I*) > 2 were classified as observed and used in the subsequent structure solution and refinement.

The positions for Ir and one of the Cl atoms were derived from the Patterson function. The remaining non-hydrogen atoms were found in the electron density map phased on these two atoms. The structure was refined by the method of least-squares, minimizing Σ*w*(|*F*<sub>o</sub>| - |*F*<sub>c</sub>|)<sup>2</sup>. The atomic scattering factors were taken from the tabulation of Cromer and Wabers<sup>8</sup> using the values for the uncharged

atoms, except for hydrogen, where the values of Stewart *et al.* were employed.<sup>9</sup> The atomic scattering factors for Ir and Cl were corrected for the effect of anomalous scattering using the values given by Cromer and Liberman.<sup>10</sup> The X-ray system<sup>11</sup> was used for the crystallographic computations and ORTEP II for the illustrations.<sup>12</sup>

After anisotropic thermal parameters were introduced for the non-hydrogen atoms the subsequent difference Fourier syntheses showed the positions of the hydrogen atoms in the structure. A common isotropic temperature factor of  $B = 3.1 \text{ \AA}^2$  was used for all the hydrogen atoms. The positional parameters for the hydrogen atoms were also included in the refinement with the exception of the hydrogen atoms of the terminal  $-\text{NH}_3^+$  group, as attempts to refine their parameters led to this group having a physically unrealistic geometry. The weights were changed from unit weights to weights of the form  $w^{-1} = \sigma^2(F) + 0.0002|F|^2$  in the final refinement cycles. This scheme gave a uniform distribution of  $\langle w\Delta F^2 \rangle$  with both  $F_o$  and  $(\sin \theta)/\lambda$ . In the final cycle the maximum shift for the 175 variables was  $0.3\sigma$ . The difference Fourier map maximum peak in the final of  $1.5 e \text{ \AA}^{-3}$  was found close to Ir. The final positional parameters are given in Table 2.

[Ir(en)(en\*)Cl<sub>3</sub>]. The orange-red crystals crystallize in the monoclinic space group  $P2_1/c$ . The lattice parameters and orientation matrix used in the data collection were obtained from a least-squares refinement of the setting angles for 15 reflections with  $11 < \theta < 15^\circ$ . MoK $\alpha$  radiation obtained from the graphite monochromator of a Syntex P2<sub>1</sub> diffractometer was used for data collection.

The intensities of two standard reflections measured after every 50 reflections had an intensity variation within  $\pm 4\%$ . The data were corrected for Lorentz, polarisation and

Table 2. Positional parameters and equivalent isotropic thermal parameters ( $\text{\AA}^2$ ) for the non-hydrogen atoms in [Ir(en)(enH)Cl<sub>3</sub>]Cl·H<sub>2</sub>O.

Atom	x	y	z	$U_{\text{eq}}^a$
Ir	0.74891(2)	0.52175(2)	0.61965(2)	0.02055
Cl1	0.63013(11)	0.41210(11)	0.74803(12)	0.0339
Cl2	0.87633(11)	0.62616(11)	0.49794(12)	0.0333
Cl3	0.60397(11)	0.67223(11)	0.57739(12)	0.0322
N1	0.8236(4)	0.6103(4)	0.7858(4)	0.028
N2	0.8826(4)	0.4023(4)	0.6731(4)	0.029
N3	0.6748(4)	0.4213(4)	0.4565(4)	0.029
N4	0.6587(6)	0.3962(4)	0.0904(5)	0.057
C1	0.9076(5)	0.5316(5)	0.8648(5)	0.033
C2	0.9711(5)	0.4603(5)	0.7712(5)	0.033
C3	0.6825(6)	0.4602(5)	0.3218(5)	0.037
C4	0.6179(6)	0.3783(5)	0.2199(5)	0.036
Cl10	0.3370(2)	0.32847(12)	0.96953(14)	0.0500
O	1.1152(5)	0.7040(4)	0.8035(5)	0.062

$$^a U_{\text{eq}} = \frac{1}{3} \sum_i U_{ii}$$

Table 3. Positional parameters and equivalent isotropic thermal parameters ( $\text{\AA}^2$ ) for the non-hydrogen atoms in [Ir(en)(en\*)Cl<sub>3</sub>].

Atom	x	y	z	$B_{\text{eq}}^a$
Ir	-0.01839(5)	0.25529(5)	0.14814(3)	2.22
Cl1	0.1427(4)	0.3364(3)	0.2757(2)	3.2
Cl2	-0.1779(4)	0.1627(3)	0.0239(2)	4.1
Cl3	-0.1687(4)	0.4617(3)	0.1388(2)	3.2
N1	0.1509(12)	0.3294(9)	0.0519(6)	2.9
N2	0.1296(11)	0.0855(9)	0.1440(6)	2.3
N3	-0.1679(12)	0.1686(10)	0.2512(7)	3.8
N4	-0.3846(15)	0.0593(13)	0.4006(8)	5.7
C1	0.2621(16)	0.2165(12)	0.0235(8)	3.5
C2	0.2905(16)	0.1232(12)	0.1052(8)	3.5
C3	-0.3322(21)	0.2102(18)	0.2659(13)	7.9
C4	-0.4455(19)	0.1403(19)	0.3260(11)	6.7

$$^a B_{\text{eq}} = \frac{1}{3} \sum_i B_{ii}$$

absorption effects. The transmission factors were determined on a relative scale and determined from the analysis of  $\Psi$ -scan data.

The structure was solved and refined as described for the structure of [Ir(en)(enH)Cl<sub>3</sub>]Cl·H<sub>2</sub>O. The hydrogen atoms were introduced in idealized positions with a common isotropic temperature factor of  $B = 5.5 \text{ \AA}^2$ . It was not possible to locate the hydrogen atoms of the monodentate ethylenediamine ligand, en\*. The scattering factors were taken from Ref. 8. The function minimized in the least-squares refinement was  $\sum w(|F_o| - |F_c|)^2$ . The calculations were performed with the Syntex XTL structure determination system on a NOVA 1200 computer.<sup>13</sup> Table 3 contains the final atomic parameters.

Anisotropic thermal parameters, parameters for the hydrogen atoms in the two structures as well as lists of observed and calculated structure amplitudes are available from the authors.

## Results and discussion

On deprotonation of the *mer*-[Ir(en)(enH)Cl<sub>3</sub>]<sup>+</sup> complex ( $\text{p}K_a = 9.12$ ; 1.0 M NaClO<sub>4</sub>, 25°C)<sup>3</sup> the *mer*-[Ir(en)(en\*)Cl<sub>3</sub>] species was produced and the compound crystallized. The reversibility of the protonation reaction was ascertained by the <sup>13</sup>C NMR spectra of the two species dissolved in acidic and alkaline solutions. Thus it was confirmed that the pendant 1,2-ethanediamine ligand remains unaltered, apart from the protonation and exchange of D for H on the amine groups in alkaline D<sub>2</sub>O solutions.

The molecular geometries of the two complexes *mer*-[Ir(en)(enH)Cl<sub>3</sub>]<sup>+</sup> and [Ir(en)(en\*)Cl<sub>3</sub>] are illustrated by the two ORTEP drawings in Figs. 1 and 2. Bond lengths and angles appear in Table 4. The coordination geometry around Ir is virtually identical in the two compounds. Within the experimental accuracy the distances between Ir

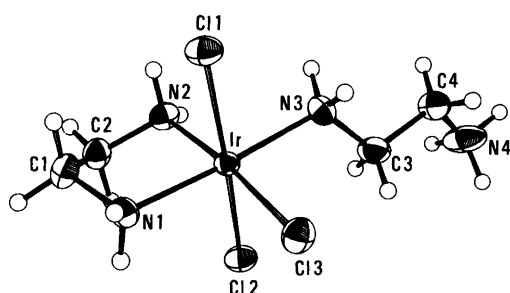


Fig. 1. ORTEP drawing of the cation  $[\text{Ir}(\text{en})(\text{enH})\text{Cl}_3]^+$  illustrating the atomic labelling.

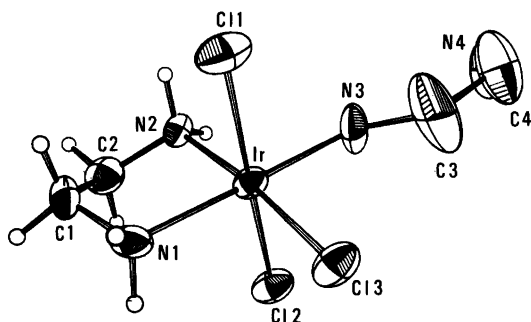


Fig. 2.  $[\text{Ir}(\text{en})(\text{en}^*)\text{Cl}_3]$  drawn as the cation in Fig. 1.

and the two *trans*-dispositioned chloride ligands, Cl1 and Cl2, are alike. This distance  $\langle \text{Ir}-\text{Cl} \rangle = 2.357(2)$  Å is, however, slightly but significantly shorter than the Ir–Cl distance to the *cis*-chloride ion,  $\langle \text{Ir}-\text{Cl} \rangle = 2.382(3)$  Å. From a simple electrostatic rationalization one would have predicted that the two *trans*-chloride ions should have the longest Ir–Cl distance. The present observation indicates that the Ir–Cl bond is not only of electrostatic origin. The Ir–N distances involving the unidentate  $\text{enH}^+$  and  $\text{en}^*$  ligands are identical in the two complexes,  $\langle \text{Ir}-\text{N} \rangle = 2.102$  Å, and longer than the Ir–N bond lengths involving the bidentate 1,2-ethanediamine ligands,  $\langle \text{Ir}-\text{N} \rangle = 2.071$  Å. The latter distances are very similar to the equivalent bonds in the hydroxo-bridged binuclear iridium(III) complex,  $\Delta, \Delta - [(\text{H}_2\text{O})(\text{en})_2\text{Ir}(\text{OH})(\text{en})_2(\text{OH})]^{4+}$ .<sup>14</sup> The only significant difference between the two Ir complexes is found in the geometry and stereochemistry of the unidentate  $\text{enH}^+$

Table 4. Bond lengths (Å) and angles (°) in the two complexes.

	$[\text{Ir}(\text{en})(\text{enH})\text{Cl}_3]^+$	$[\text{Ir}(\text{en})(\text{en}^*)\text{Cl}_3]$
Ir–Cl1	2.3593(14)	2.358(3)
Ir–Cl2	2.3539(13)	2.357(3)
Ir–Cl3	2.3805(13)	2.384(3)
Ir–N1	2.060(4)	2.088(9)
Ir–N2	2.066(4)	2.068(9)
Ir–N3	2.103(4)	2.101(10)
N1–C1	1.475(7)	1.497(15)
N2–C2	1.488(7)	1.474(15)
C1–C2	1.505(8)	1.45(2)
N3–C3	1.456(7)	1.42(2)
N4–C4	1.470(8)	1.41(2)
C3–C4	1.513(8)	1.44(2)
C1–Ir–Cl2	176.9(2)	176.99(11)
C2–Ir–Cl3	91.16(4)	91.00(11)
C1–Ir–Cl3	91.65(4)	91.58(10)
C1–Ir–N1	90.50(13)	91.2(3)
C1–Ir–N2	88.83(13)	89.1(3)
C1–Ir–N3	87.21(13)	85.6(3)
C2–Ir–N1	88.16(12)	90.4(3)
C2–Ir–N2	88.23(13)	88.6(3)
C2–Ir–N3	94.00(13)	92.6(3)
C3–Ir–N1	90.95(12)	90.3(3)
C3–Ir–N2	173.8(3)	173.2(3)
C3–Ir–N3	91.86(12)	95.0(3)
N1–Ir–N2	82.9(2)	83.0(3)
N1–Ir–N3	176.4(3)	173.9(4)
N2–Ir–N3	94.3(2)	91.8(4)
Ir–N1–C1	109.7(3)	108.7(7)
N1–C1–C2	108.2(4)	109.8(9)
C1–C2–N2	108.2(4)	108.6(10)
C2–N2–Ir	108.6(3)	108.9(7)
Ir–N3–C3	121.3(3)	122.8(9)
N3–C3–C4	112.5(5)	124.1(15)
C3–C4–N4	110.4(5)	119.8(14)
Torsion angles		
N3–C3–C4–N4	–161.3(5)	25(2)
N1–C1–C2–N2	–52.5(5)	50.9(12)

and  $\text{en}^*$  ligands. They attain different conformations. In the  $\text{enH}^+$  complex, the conformation can be described as *sym-trans* compared to the *sym-cis* conformation found in the  $\text{en}^*$  complex. The bond lengths also exhibit some discrepancies. The bond lengths found in the  $\text{en}^*$  group are all shorter than the equivalent values observed in the  $\text{enH}^+$  ligand. This difference seems to be due to some conformational disorder of the  $\text{en}^*$  group, which would lead to an apparent bond length shortening. This is supported by the large thermal vibrations of the  $\text{en}^*$  group and the fact that the positions of the hydrogen atoms of this group are not well-defined. The alternative explanation that the C3–C4 bond in the  $\text{en}^*$  group should have some double-bond character is precluded on the basis of the NMR spectra. The molecular dimensions of the  $\text{enH}^+$  ligand are very similar to those found in the two Pt(II) and Pt(IV) complexes investigated earlier. The  $\text{enH}^+$  group is found in

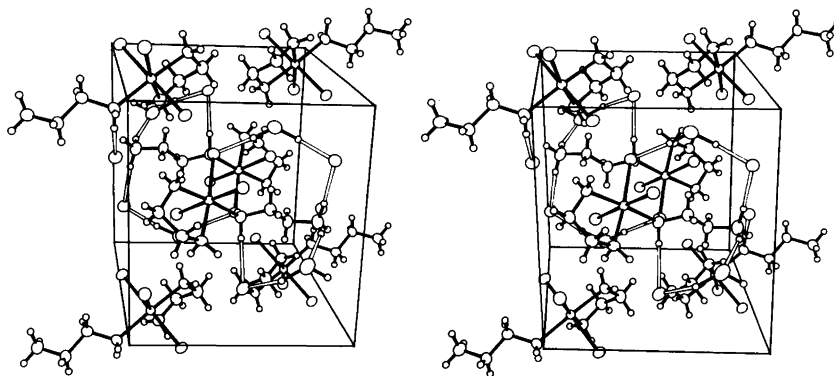


Fig. 3. Stereoscopic pair illustrating the packing in [Ir(en)(enH)Cl<sub>3</sub>]Cl·H<sub>2</sub>O. The open bonds designate the hydrogen bonds in the structure.

Table 5. Possible hydrogen bonds in [Ir(en)(enH)Cl<sub>3</sub>]Cl·H<sub>2</sub>O.

D-	H---	A	D-A/Å	D-H-A°
N4	H2(N4)	Cl10 <sup>a</sup>	3.159(5)	165(5)
N4	H3(N4)	O <sup>b</sup>	2.923(8)	149(6)
O	H1(O)	Cl3 <sup>c</sup>	3.139(5)	174(5)
O	H2(O)	Cl10 <sup>d</sup>	3.226(5)	162(4)

<sup>a</sup>(1-x, 1-y, 1-z). <sup>b</sup>(2-x, 1-y, 1-z). <sup>c</sup>(½+x, 1½-y, 1½+z).  
<sup>d</sup>(1½-x, 1½+y, 1½-z).

different conformations in the two Pt complexes. In [Pt(enH)Cl<sub>3</sub>] the ligand enH<sup>+</sup> is *trans*,<sup>5</sup> and in [Pt(enH)Cl<sub>3</sub>] it adopts a *gauche* conformation,<sup>6</sup> the torsion angle N-C-C-N being 73°. These variations in the conformation of unidentate enH<sup>+</sup> and en\* groups appear to be connected with the intermolecular hydrogen-bonding structures. In the crystal structure of [Ir(en)(en\*)Cl<sub>3</sub>] no hydrogen bonds are observed, compared with the crystal structure of [Ir(en)(enH)Cl<sub>3</sub>]Cl·H<sub>2</sub>O, where the complex cations are linked by hydrogen bonds to the uncoordinated chloride and the water molecule, as illustrated in the stereoscopic pair in Fig. 3 and by the list of hydrogen bonds in Table 5.

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