The Preparation and Characterization of Some Chloro(1,2-ethanediamine)iridium(III) Species

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An investigation of a published procedure for the preparation of *cis*- and *trans*-[Ir(en)$_2$Cl$_2$]Cl (en = 1,2-ethanediamine) revealed that besides these species also [Ir(en)Cl$_4$]$^-$ and the hitherto unknown *mer*-[Ir(en)(enH)Cl$_3$]$^+$ (enH$^+$ = 2-aminoethylammonium ion) are formed. The latter is assigned as the meridional geometrical isomer by comparison of the absorption spectrum with that calculated using the angular overlap model. A modified procedure for the isolation of the *cis*- and *trans*-isomers in a yield of *ca.* 40 % for each is given. The slightly soluble *trans*-[Ir(en)$_2$Cl$_2$]$_3$[IrCl$_6$].H$_2$O has also been prepared. In addition to chemical analysis the compounds have been characterized by thermogravimetry and by their electronic spectra. The concentration acidity constant of *mer*-[Ir(en)(enH)Cl$_3$]$^+$ is estimated to be $10^{-9.12 \pm 0.04}$ mol/l (25 °C, 1 M NaClO$_4$).

A survey of the published methods[1–4] for the preparation of *cis*- and *trans*-dichlorobis(1,2-ethanediamine)iridium(III) shows that the preparations are cumbersome and/or give low yields. We considered that the procedure published by Baranovskii *et al.*[2] was the most promising and tried to reproduce it. However, both the *cis*- and *trans*-isomers isolated by this method were contaminated with red by-products which were very difficult to remove by crystallization. We therefore examined the products of the reaction by chromatography on a cation exchanger. In addition to *cis*- and *trans*-[Ir(en)$_2$Cl$_2$]$^+$ (en = 1,2-ethanediamine) the mixture contained [Ir(en)Cl$_4$]$^-$ and also the hitherto unknown *mer*-[Ir(en)(enH)Cl$_3$]$^+$ (enH$^+$ = 2-aminoethylammonium ion). A procedure is given for the isolation of these compounds.

Furthermore, an alternative method has been developed for the isolation of pure *cis*- and *trans*-[Ir(en)$_2$Cl$_2$]Cl in a yield of *ca.* 40 % for each and the slightly soluble olive green *trans*-[Ir(en)$_2$Cl$_2$]$_3$[IrCl$_6$].H$_2$O has been prepared by metathesis. The compounds were identified by chemical analysis, by their electronic spectra and by thermogravimetry.

EXPERIMENTAL

Materials. Iridium(III) chloride hydrate (*ca.* 6.6 mol H$_2$O/mol Ir) was obtained from Johnson, Matthey and Co. and 1,2-ethanediamine ("*puriss. p.a.*") from Fluka. All other chemicals were of analytical or reagent grade and were used without further purification.

Instrumentation. Absorption spectra were recorded on a Cary 118C spectrophotometer. Thermogravimetric measurements were performed on the thermobalance described by Pedersen.[5]

Synthetic Procedures

1. cis- and trans-[Ir(en)$_2$Cl$_2$]$^+$, mer-[Ir(en)(enH)Cl$_3$]$^+$ and [Ir(en)Cl$_4$]$^-$. A 6.40 g sample of IrCl$_3$.6.6H$_2$O (15.3 mmol) is dissolved in 50 ml of water by heating to boiling in a 250 ml flask fitted with a condenser. Then a mixture of 2.6 ml of 1,2-ethanediamine (39 mmol) and 4.4 ml of acetic acid (77 mmol) diluted to 50 ml with water is added with reflux over a period of *ca.* 10 min. The refluxing is continued for a further 10 h after which the reddish brown reaction mixture is filtered, and the filter washed thoroughly with water. The filtrate and washings are evaporated to dryness on a rotating vacuum evaporator, RVE, (final bath temperature 50 °C), and the residue is dissolved in 20 ml of boiling water. 25 ml of 12 M HCl are added to the hot

solution (if the solution is boiled an olive green precipitate of the slightly soluble *trans*-[Ir(en)$_2$Cl$_2$]$_3$[IrCl$_6$].H$_2$O is formed) and the solution is again evaporated to dryness on an RVE (final bath temperature 90 °C).

The orange residue is dissolved in 10 ml of boiling water. The solution is allowed to stand for crystallization, first at room temperature, then in the refrigerator overnight, and is finally cooled in ice. The orange crystals are filtered and washed, first with two 1 ml portions of ice-cold water, then with ethanol, finally with ether, and dried in air (product A). The filtrate and washings are evaporated to dryness on an RVE (final bath temperature 50 °C). The residue is boiled with 5 ml of water, and 7.5 ml of 12 M HCl are added. The solution is allowed to stand for crystallization, first at room temperature, then in the refrigerator overnight, and is finally cooled in ice. The crystals are filtered and washed, first with two 1 ml portions of ice-cold 6 M HCl, then with ethanol, finally with ether, and dried in air (product B).

The products A and B (*ca.* 6 g) are mixed and dissolved in 500 ml of water and 12 M HCl is added until pH = *ca.* 2 (*ca.* 0.4 ml). The solution is filtered and the filtrate is applied on a column of 30 g of SP-Sephadex C-25 cation exchanger (Li$^+$-form, *ca.* 60 cm long and *ca.* 2 cm diameter) which is then washed with water until the eluate which contains the red [Ir(en)Cl$_4$]$^-$, fraction I, is colourless. The column is then eluted with 0.02 M LiOH, which will neutralize [Ir(en)(enH)Cl$_3$]$^+$ (usually more than 500 ml are necessary) and the golden coloured fraction II containing [Ir(en)(en*)Cl$_3$] (en* = unidentate 1,2-ethanediamine) is collected. The column is then washed with 200 ml of water and finally the yellow band, containing *cis*- and *trans*-[Ir(en)$_2$Cl$_2$]$^+$, is eluted with 0.25 M LiCl. The yellow fraction III is collected.

Fraction I is acidified with 2 ml of 12 M HCl, before it is evaporated to a volume of *ca.* 10 ml.* Then 3 ml of 2 M KOH are added and the solution is evaporated to dryness on an RVE (final bath temperature 50 °C). LiCl and HCl are extracted by boiling with 20 ml of absolute ethanol followed by filtration and washing with absolute ethanol. The residue is dissolved in the minimum volume (*ca.* 5 ml) of boiling 0.1 M HCl and the solution is allowed to stand overnight for crystallization. The precipitate is filtered and washed, first with two 0.5 ml portions of ice-cold water, then with ethanol,

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* If the solution is not acidic the pink compound (Ir(en)Cl$_3$)$_x$ is precipitated.[11] This compound can be reconverted to [Ir(en)Cl$_4$]$^-$ by boiling with 2 M HCl. In the analytical data for (Ir(en)Cl$_3$)$_x$ given in Ref. 11 it seems likely that the values found for C and N have been interchanged.

finally ether, and dried in air. Yield 0.7 g (10 %) of reddish orange K[Ir(en)Cl$_4$].2H$_2$O. (Found: C 5.17; H 2.47; N 5.88; Cl 30.45; K 8.29. Calc. .for KIrC$_2$H$_{12}$N$_2$Cl$_4$O$_2$: C 5.12; H 2.58; N 5.97; Cl 30.22; K 8.33). Thermogravimetry: loss of weight 81.0 mg/g sample, *i.e.* 38.2 g/mol.

Fraction II is acidified with HCl and evaporated to dryness on an RVE (final bath temperature 50 °C). LiCl is extracted by boiling with 20 ml of absolute ethanol followed by filtration and washing with absolute ethanol. The residue is dissolved in the minimum volume (*ca.* 3 ml) of boiling water and the solution is allowed to stand overnight for crystallization. The precipitate is filtered, washed with two 1 ml portions of ice-cold water, and dried in air. Yield 1.5 g (21 %) of orange *mer*-[Ir(en)(enH)Cl$_3$]Cl.H$_2$O. (Found: C 10.17; H 3.86; N 11.94; Cl(tot.) 29.18; Cl(ion.) 7.55. Calc. for IrC$_4$H$_{19}$N$_4$Cl$_4$O: C 10.15; H 4.05; N 11.84; Cl(tot.) 29.97; Cl(ion.) 7.49). Thermogravimetry: loss of weight 39.0 mg/g sample, *i.e.* 18.5 g/mol.

Fraction III is acidified with HCl and evaporated to dryness on an RVE (final bath temperature 50 °C). LiCl is extracted by boiling with 30 ml of absolute ethanol followed by cooling, filtration, and washing with absolute ethanol. The residue is dissolved in the minimum volume (*ca.* 4 ml) of boiling water and the solution is allowed to stand overnight for crystallization. The precipitate is filtered, washed with 1 ml of ice-cold water, and dried in air. Yield 1.5 g (22 %) of pale yellow *cis*-[Ir(en)$_2$Cl$_2$]Cl.H$_2$O. (Found: C 11.04; H 4.25; N 12.79; Cl(tot.) 24.60; Cl(ion.) 8.16. Calc. for IrC$_4$H$_{18}$N$_4$Cl$_3$O: C 11.00; H 4.15; N 12.83; Cl(tot.) 24.35; Cl(ion.) 8.12). Thermogravimetry: loss of weight 48.4 mg/g sample, *i.e.* 21.3 g/mol.

The filtrate and washings are heated to boiling and 1.5 volumes of 12 M HCl are added. The solution is allowed to stand at room temperature for crystallization, and is finally cooled in ice. The precipitate (*trans*-[Ir(en)$_2$Cl$_2$]Cl.HCl.2H$_2$O) is filtered and washed, first with two 0.5 ml portions of 6 M HCl, then with ethanol, finally with ether, and dried at 135 °C. Yield 0.8 g (12 %) of yellow *trans*-[Ir(en)$_2$Cl$_2$]Cl. (Found: C 11.51; H 3.92; N 13.39; Cl(tot.) 25.35; Cl(ion.) 8.51. Calc. for IrC$_4$H$_{16}$N$_4$Cl$_3$: C 11.47; H 3.85; N 13.38; Cl(tot.) 25.40; Cl(ion.) 8.47). By recrystallization from water (*ca.* 0.6 ml/g) the monohydrate is obtained. Anal. IrC$_4$H$_{18}$N$_4$Cl$_3$O: C, H, N, Cl(tot.), Cl(ion.). Thermogravimetry: loss of weight 42.7 mg/g sample, *i.e.* 18.7 g/mol.

2. Dichlorobis(1,2-ethanediamine)iridium(III) chlo-rides. A 6.40 g sample of IrCl$_3$.6.6H$_2$O (15.3 mmol) is dissolved in a mixture of 0.9 ml of acetic acid (16 mmol) and 17 ml of water by heating to boiling in a 50 ml flask fitted with a condenser. Then 3.1 ml of 1,2-ethanediamine (46 mmol), diluted to 6 ml with water, are added with reflux: first 1 ml then 0.5 ml

every half hour. After the last addition the solution is refluxed for further 5 h and then evaporated to dryness on an RVE (final bath temperature 90 °C). The solid brown residue is heated to 170 °C for 24 h and is then dissolved in 20 ml of boiling water. The solution is filtered, flask and filter are washed with two 10 ml portions of boiling water, and the filtrate and washings are evaporated to dryness on an RVE. The residue is dissolved in 10 ml of boiling water and the solution is allowed to stand for crystallization, first 2 h at room temperature then in the refrigerator overnight. The crystal cake is then broken up and the mixture is cooled in ice-water for 3 h before the crystals are filtered, washed with two 1 ml portions of ice-cold water, and dried in air. Yield 2.5 g (37 %) of cis-[Ir(en)$_2$Cl$_2$]Cl.H$_2$O.* Anal. IrC$_4$H$_{18}$N$_4$Cl$_3$O: C, H, N, Cl(tot.), Cl(ion.).

The combined filtrate and washings are heated to boiling, 20 ml of 12 M HCl are added, and the mixture is allowed to stand at room temperature for 1 h before it is cooled in ice for 2 h. The crystals are filtered and washed, first with two 3 ml portions of ice-cold 6 M HCl,** then with ethanol, finally with ether. The yellow product is dried at 135 °C. Yield 2.5 g (39 %) of trans-[Ir(en)$_2$Cl$_2$]Cl. Anal. IrC$_4$H$_{16}$N$_4$Cl$_3$: C, H, N, Cl.

3. trans-*Dichlorobis(1,2-ethanediamine)iridium(III) hexachloroiridate(III), monohydrate.* 10 ml of 12 M HCl are added to a solution of 0.25 g of IrCl$_3$.6.6H$_2$O (0.60 mmol) in 5 ml of boiling water. The mixture is heated to boiling and a hot solution of 0.75 g of trans-[Ir(en)$_2$Cl$_2$]Cl (1.8 mmol) in 5 ml of water is added. The solution is heated to boiling and then allowed to stand overnight for crystallization. The olive green precipitate is then filtered, washed thoroughly with water, and dried in air. Yield 0.82 g (87 %) of trans-[Ir(en)$_2$Cl$_2$]$_3$[IrCl$_6$].H$_2$O. (Found: C 9.16; H 3.28; N 10.71; Cl 27.38. Calc. for Ir$_4$C$_{12}$H$_{50}$N$_{12}$Cl$_{12}$O: C 9.16; H 3.20; N 10.69; Cl 27.05). Thermogravimetry: loss of weight 15.0 mg/g sample, i.e. 23.6 g/mol.

RESULTS AND DISCUSSION

The content of water (and HCl) of crystallization was determined by thermogravimetry. Fig. 1 shows the results for trans-[Ir(en)$_2$Cl$_2$]Cl.HCl.2H$_2$O and

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* Both (+)-α-bromocamphor-π-sulfonic acid and (+)$^{RD}_{546}$-ethylenediaminetetraacetatocobaltate(III) have been reported [4,9] as resolving agents for cis-[Ir(en)$_2$Cl$_2$]$^+$.

** If the washing with ethanol and ether is omitted and the product is dried in air, trans-[Ir(en)$_2$Cl$_2$]Cl.HCl.2H$_2$O is obtained. Yield 2.6 g (39 %). (Found: C 9.65; H 4.23; N 11.43; Cl(tot.) 28.62; Cl(ion.) 14.44; H$^+$ 2.037 mmol/g. Calc. for IrC$_4$H$_{21}$N$_4$Cl$_4$O$_2$: C 9.78; H 4.31; N 11.41; Cl(tot.) 28.87; Cl(ion.) 14.43; H$^+$ 2.036 mmol/g). Thermogravimetry: loss of weight 155 mg/g sample, i.e. 76.7 g/mol.
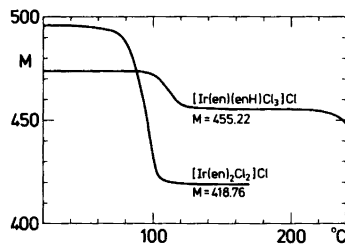
Fig. 1. Thermogravimetric analysis of trans-[Ir(en)$_2$Cl$_2$]Cl.HCl.2H$_2$O and mer-[Ir(en)(enH)Cl$_3$]-Cl.H$_2$O in air. Heating rate 2 °C/min. The ordinate gives a number which is proportional to the sample weight, so that the value at the plateau to the right equals the molecular weight of the material without water (and HCl) of crystallization.

mer-[Ir(en)(enH)Cl$_3$]Cl.H$_2$O. The curves for the other three compounds are similar in shape. The compounds start to loose water of crystallization at the following approximate temperatures: K-[Ir(en)Cl$_4$].2H$_2$O: 50 °C, cis- and trans-[Ir(en)$_2$Cl$_2$]-Cl.H$_2$O: 60 °C, and trans-[Ir(en)$_2$Cl$_2$]$_3$[IrCl$_6$].H$_2$O: 45 °C.

The absorption spectra of cis- and trans-[Ir(en)$_2$Cl$_2$]Cl.H$_2$O are shown in Fig. 2. They are in good agreement with earlier published results.[1,4,6-10] Fig. 3 shows the absorption spectra of K[Ir(en)Cl$_4$].2H$_2$O and mer-[Ir(en)(enH)Cl$_3$]-Cl.H$_2$O. Baranovskii et al.[11] reports maxima at 320, 369 and 498 nm for the former. The latter compound is assigned as the meridional geometrical isomer by comparison of the absorp-
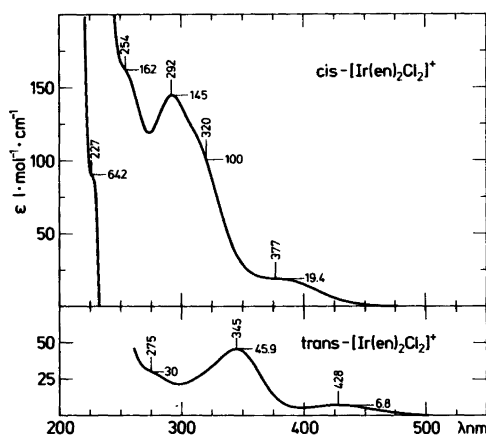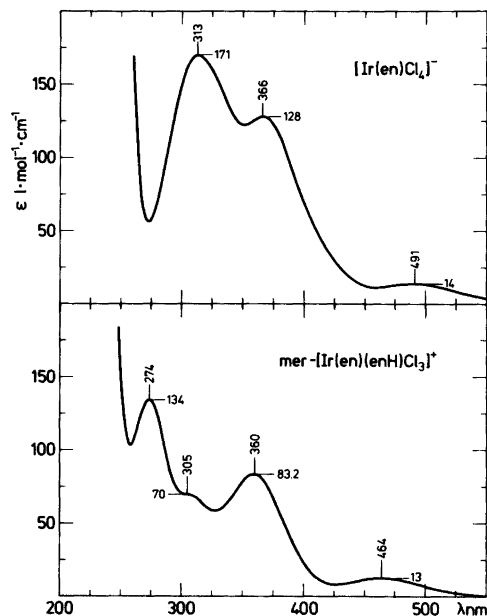

Fig. 2. The absorption spectra of cis- and trans-[Ir(en)$_2$Cl$_2$]Cl.H$_2$O.

Fig. 3. The absorption spectra of $K[Ir(en)Cl_4].2H_2O$ and *mer*-$[Ir(en)(enH)Cl_3]Cl.H_2O$.

tion spectrum with the transitions calculated using the angular overlap model (Fig. 4). The calculations of the transition energies are based on the expanded radial function model[12] for the d^6 system, where the energy level $^1A_{1g}(O_h)$ is assigned the t_{2g}^6 configuration and both $^1T_{1g}(O_h)$ and $^1T_{2g}(O_h)$ the t_2^5e configuration. The center of gravity rule is lost, because of the non-diagonal elements between $^1T_{1g}(O_h)$ and $^1T_{2g}(O_h)$, which have been taken into account in this model. The connecting lines show the cubic parentage of the energy levels. The holohedric symmetry D_{4h} for *cis*-N_4Cl_2 and *cis*-N_2Cl_4 and O_h for *fac*-N_3Cl_3 accounts for the degeneracies of the energy levels. As seen from Fig. 4, there is a reasonably good agreement between the calculated and the observed transition energies. It should be noted that in the *cis*-N_2Cl_4 case, the calculations show an absorption band at 36.7×10^3 cm^{-1} (272 nm), where the spectrum (Fig. 3) shows a very narrow minimum; however, only 1000 cm^{-1} uncertainty in the calculations would change the calculated value to 37 700 cm^{-1} (265 nm) or 35 700 cm^{-1} (280 nm) and at both these places the experimental spectrum could accommodate a band
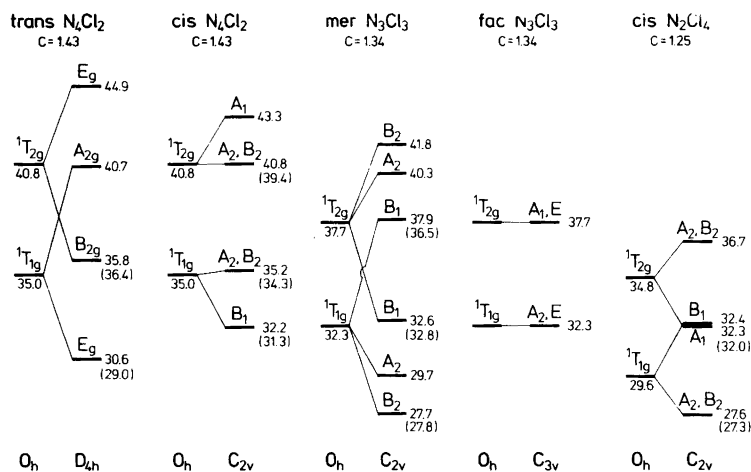

Fig. 4. Comparison of calculated and experimental (in parentheses) transition energies for some $[IrN_xCl_{6-x}]^{x-3}$ species. All energies in the figure are given in 1000 cm^{-1} units. The calculated values were obtained by using the angular overlap model matrices published by Schäffer and Jørgensen,[12] the relations $\Delta = \sigma + C = \Delta_\sigma - \Delta_\pi$, $C = 4B$, $\Delta_\sigma = 3e'_\sigma$, and $\Delta_\pi = 4e'_\pi$ and the following parameters $\sigma_{Cl_6} = 24.1 \times 10^3$ cm^{-1} (Ref. 14), $B_{Cl_6} = 265$ cm^{-1}, and $\Delta_{\pi Cl} = 1 \times 10^3$ cm^{-1} *i.e.* $\Delta_{\sigma Cl} = 26.2 \times 10^3$ cm^{-1}, and $\sigma_{N_6} = 40.5 \times 10^3$ cm^{-1} (Ref. 15), $B_{N_6} = 405$ cm^{-1}, and $\Delta_{\pi N} = 0$ *i.e.* $\Delta_{\sigma N} = 42.1 \times 10^3$ cm^{-1}. The $C_{N_xCl_{6-x}}$-values have been calculated by linear interpolation between the C_{Cl_6} — and C_{N_6} —values.

Table 1. Concentration acidity constants of the 1,2-ethanediammonium ion and of various complexes containing the 2-aminoethylammonium moiety.

Acid	pK_a	Medium	Ref.
enH$^+$	10.17	1 M KNO$_3$	18
	10.06	1 M KCl	19
	10.16	1 M NaCl	20
	10.03	I=0.1 M	21
enH$_2^{2+}$	7.49	1 M KNO$_3$	18
	7.44	1 M KCl	19
	7.52	1 M NaCl	20
	7.22	I=0.1 M	21
Ag(enH)$^{2+}$	8.98	I=0.1 M	21
Hg(enH)$^{3+}$	8.2	1 M KNO$_3$	18
(NH$_3$)$_5$CrOCr(NH$_3$)$_4$(enH)$^{5+}$	8.42	0.1 M KCl	22
(NH$_3$)PtCl$_2$(enH)$^+$	*ca.* 7	1 M KCl	23
Cr(en)$_2$(OH)(enH)$^{3+}$	8.8	0.25 M NH$_4$Cl	20
mer-Ir(en)Cl$_3$(enH)$^+$	9.12	1 M NaClO$_4$	This work

component. The B values were estimated from the complete d^6 matrices for O_h-symmetry,[13] assuming $C=4B$ and using the first ($^1A_{1g}\rightarrow{}^1T_{1g}$) and second ($^1A_{1g}\rightarrow{}^1T_{2g}$) transition energies 24.1×10^3 cm^{-1} and 28.1×10^3 cm^{-1} (Ref. 14) for [IrCl$_6$]$^{3-}$ and 40.5×10^3 cm^{-1} (Ref. 15) for [Ir(en)$_3$]$^{3+}$ and 46.7×10^3 cm^{-1} (Ref. 16) for [Ir(NH$_3$)$_6$]$^{3+}$. We have used the energy of the second spin allowed transition band for [Ir(NH$_3$)$_6$]$^{3+}$, firstly, because the $^1A_{1g}\rightarrow{}^1T_{2g}$ transition for [Ir(en)$_3$]$^{3+}$ only appears as a shoulder in the spectrum,[15] secondly, because in both the analogous CoN$_6$ and RhN$_6$ chromophores of d^6 configuration the $^1A_{1g}\rightarrow{}^1T_{2g}$ transition is observed at the same energy.

An X-ray crystal structure analysis of [Ir(en)(enH)Cl$_3$]Cl.H$_2$O is presently being made.

The concentration acidity constant of *mer*-[Ir(en)(enH)Cl$_3$]$^+$ (1.0 M NaClO$_4$, 25.0 °C) was estimated to be $10^{-9.12\pm0.04}$ mol/l by regression analysis of the titration data as described by Mønsted and Mønsted.[17] A comparison with relevant literature data is shown in Table 1.

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