Iridium(III) Complexes of Macrocyclic Ligands. Preparation and Characterization of Iridium(III) Complexes of 1,4,8,11-Tetraazacyclotetradecane

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The reaction between $IrCl_3 \cdot aq$ or $Ir(thtp)_3Cl_3$ (thtp = tetrahydrothiophene) and 1,4,8,11-tetraazacyclotetradecane (cyclam) gives compounds which allow the isolation of both cis- and trans-$[Ir(cyclam)Cl_2]Cl$. Absorption spectra, ^{13}C NMR spectra and X-ray diffraction powder diagrams tentatively assign the isolated complexes to have the $(R,R,R,R/S,S,S,S)$-cis and the (R,R,S,S)-trans configuration, respectively. Complexes containing oxidized cyclam ligands with carbon–nitrogen double bonds have also been isolated from the preparative mixtures.

Recent decades have seen an increasing interest in complexes of the macrocyclic 1,4,8,11-tetraazacyclotetradecane (cyclam) ligand, and most of the transition metals have been coordinated to this ligand.[1] The complexes isolated apparently indicate a preference for the formation of trans complexes, with the five-membered chelate rings in gauche and the six-membered chelate rings in chair conformations, respectively. With reference to the chirality of the coordinated nitrogen atoms this is an (R,R,S,S)-trans conformation. For some robust systems including chromium(III),[2] cobalt(III),[3] rhodium(III)[4] and ruthenium(III),[5,6] or very large cations such as molybdenum(III),[7] it has been possible to isolate complexes having a cis configuration. Except for molybdenum(III), however, given the proper conditions, isomerization to apparently more stable trans complexes takes place. The isolated cis complexes have all been found to have the five-membered chelate rings in gauche and the six-membered chelate rings in chair conformations, as seen for the most stable trans conformation. This conformation can be referred to as an $(R,R,R,R/S,S,S,S)$-cis conformation. The above two amine ligand conformations of the trans and cis configurations are those which are supposed to be less strained and therefore sterically most probable.[3]

For iridium(III) only one paper concerning cyclam complexes has apparently been published.[8] cis-$[Ir(cyclam)Cl_2]ClO_4$ is reported to be formed by slow addition of about equimolar amounts of cyclam and $Na_2[IrCl_6]$ to boiling methanol followed by prolonged heating, methanol evaporation, dissolution in hydrochloric acid and precipitation with aqueous $NaClO_4$

solution. trans-$[Ir(cyclam)Cl_2]ClO_4$ was obtained from the cis isomer by high-temperature isomerization using nitrite, followed by base hydrolysis, chloride ion anation in hydrochloric acid and precipitation with aqueous sodium perchlorate.

The configurational assignment was assessed using IR spectroscopic data in combination with similar data for analogous ruthenium(III) complexes. UV/VIS spectral data are also indicative of the configuration around the iridium(III) centre.[9,10] The data reported for the iridium(III)–cyclam complexes are, however, very different from those of the analogous ammonia and 1,2-ethanediamine complexes, particularly with respect to the molar absorption coefficients. This is not seen for analogous sets of complexes of other metal ions. One possible reason for this difference could be that other conformational isomers were obtained for iridium(III) than for the other trivalent metal ions; however, it could also be that the preparative method starting from an iridium(IV) complex could give complexes containing an oxidized cyclam ligand.

The present paper reports the preparation and characterization of cis- and trans-$[Ir(cyclam)Cl_2]Cl$ by alternative preparative routes involving the reaction between cyclam and $IrCl_3 \cdot aq$ in water or $Ir(thtp)_3Cl_3$ (thtp = tetrahydrothiophene) in dimethyl sulfoxide.

Results and discussion

Preparations. Complexes of iridium(III) are known for their extreme robustness. This is a complicating feature of their preparative chemistry, which therefore involves the use of extreme temperatures, the introduction of labilizing ligands in the coordination sphere or the use of suitable

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catalysts. The latter method is sometimes feasible by introduction of suitable reductants which give more labile iridium(I) complexes. The possibility of reduction to iridium metal is, however, a limitation to this approach.

Ir(thtp)$_3$Cl$_3$ has been found to be an excellent starting material for the preparation of cyclam complexes of iridium(III). trans-[Ir(cyclam)Cl$_2$]Cl is formed in good yield by directly reacting the tetrahydrothiophene complex and the cyclam ligand in DMSO at elevated temperatures. Minor amounts of the cis isomer are also formed by this method, in addition to complexes of oxidized cyclam ligand.

Larger amounts of cis-[Ir(cyclam)Cl$_2$]Cl are more conveniently prepared from iridium(III) chloride and the cyclam ligand in water at high temperature. This method has several drawbacks, however, including the formation of significant quantities of polymeric material in addition to iridium reduction to the free metal apparently accompanied by oxidation of the cyclam ligand.

Complexes of oxidized cyclam ligand with one carbon–nitrogen double bond (imine–cyclam) were characterized from the products of both of the above methods.

Structural assignments. The absorption spectra of cis- and trans-[Ir(cyclam)Cl$_2$]Cl are shown in Figs. 1 and 2. A configurational assignment of these isomers has been made by comparison of the spectra in Figs. 1 and 2 with those of the analogous ammonia[9] and 1,2-ethanediamine[10] iridium(III) complexes.

The X-ray diffraction powder diagrams of trans-[Ir(cyclam)Cl$_2$]CF$_3$SO$_3$ and of cis-[Ir(cyclam)Cl$_2$]Cl show patterns similar to those of the stoichiometrically analogous chromium(III) compounds for which the (R,R,S,S)-trans and the (R,R,R,R/S,S,S,S)-cis configurations have been established through single-crystal structural studies of trans-[Cr(cyclam)(OCONH$_2$)$_2$]ClO$_4$ · 1½H$_2$O[11] and cis-[Cr(cyclam)Cl$_2$]ClO$_4$.[12]
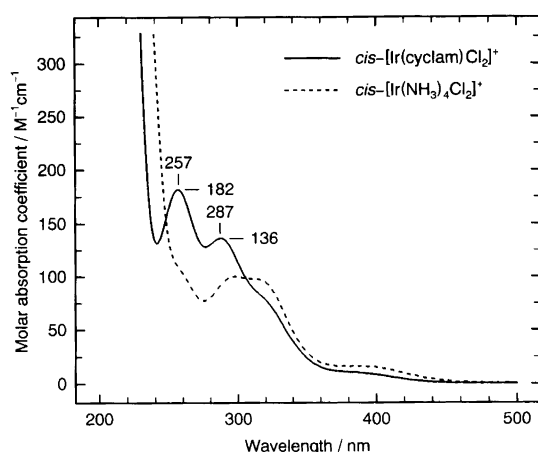
Fig. 1. Absorption spectra of cis-[Ir(cyclam)Cl$_2$]Cl and cis-[Ir(NH$_3$)$_4$Cl$_2$]Cl · ½H$_2$O[9] in water. cis-[Ir(cyclam)Cl$_2$]ClO$_4$ from Ref. 8 is reported to have shoulders at 285 and 250 nm, with molar absorption coefficients 550 and 820 M^{-1} cm^{-1}, respectively.

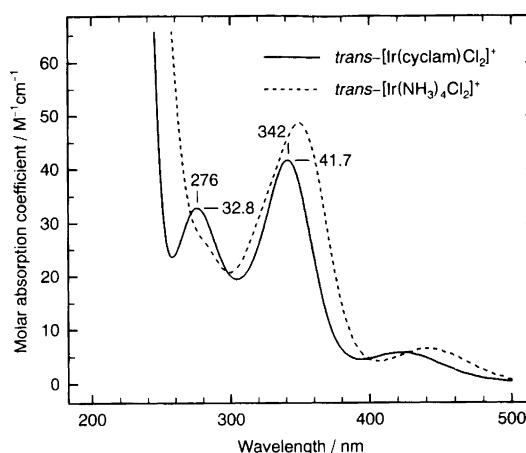Fig. 2. Absorption spectra of trans-[Ir(cyclam)Cl$_2$]Cl and trans-[Ir(NH$_3$)$_4$Cl$_2$]Cl · H$_2$O[9] in water. trans-[Ir(cyclam)Cl$_2$]ClO$_4$ from Ref. 8 is reported to have bands at 334 and 264 nm and a shoulder at 285 nm, with molar absorption coefficients 110, 285 and 220 M^{-1} cm^{-1}, respectively.

The ^{13}C NMR spectra of cis- and trans-[Ir(cyclam)Cl$_2$]Cl show five and three resonances, respectively. This is as expected for the amine ligand conformations assigned on the basis of the comparative use of the X-ray powder diffraction patterns: The cis isomer has a C$_2$-axis which makes pairs of carbon atoms identical in a ^{13}C NMR spectrum. The trans isomer has both a C$_2$-axis and a σ$_h$ mirror plane, and this results in three inequivalent carbon atoms as in the free ligand.

Complexes of oxidized cyclam ligands. Column chromatography of mixtures prepared from the cyclam ligand and iridium(III) chloride in water gives two bands of apparently singly charged species. The second band contains pure cis-[Ir(cyclam)Cl$_2$]$^+$, and the chromatographic behaviour consequently suggests a trans configuration for the components of the first band. Solid compounds could be obtained by precipitation as perchlorates. FPLC chromatography of such compounds shows several components, and ^{13}C NMR spectroscopy shows a considerable number of resonances which could be ascribed to CH$_2$ groups. Resonances are also present at higher δ-values in the region for carbon atoms double-bonded to nitrogen atoms. Fractional crystallization from hydrochloric acid solution reduced the number of com-
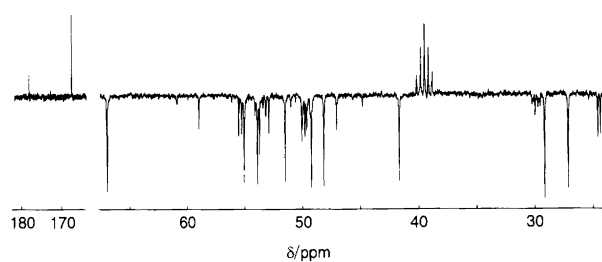

Fig. 3. ^{13}C NMR DEPT spectrum of trans-[Ir(imine–cyclam)-Cl$_2$]ClO$_4$ in DMSO.

ponents in the mixture considerably, and gave ultimately a product for which the ^{13}C NMR DEPT spectrum is given in Fig. 3. Ten major resonances are seen, of which nine are placed at the $24 < \delta < 67$ ppm region, and identified as CH_2 groups. One large peak at $\delta = 167.3$ ppm is identified as a CH group. A number of additional but smaller peaks, including one situated at $\delta = 177.9$ ppm, are also present. A likely interpretation of this spectrum is therefore that the partially purified compound is a mixture of two isomers of oxidized cyclam ligands in which one carbon–nitrogen double bond has been introduced. Lack of material prevented further purification and investigation of the complexes of oxidized cyclam ligands.

Spectral properties. The d–d transitions of the present cyclam complexes are similar to those of the analogous ammonia complexes of iridium(III), with respect to both intensities and positions of the absorption bands,[9] cf. Figs. 1 and 2. A comparison of the spectra, however, reveals a notable difference in that there is a well defined absorption band at the edge of the charge-transfer band in the macrocyclic complexes. This band is seen as shoulders only in the ammonia and 1,2-ethanediamine complexes. The reason for this difference is not obvious on the basis of data presently available. The iridium(III) cyclam complexes prepared in Ref. 8 were characterized by UV/VIS absorption spectra significantly different from those presented in Figs. 1 and 2. The molar absorption coefficients in Ref. 8 are significantly higher, and the d–d transitions in the cis complex are reported to appear as shoulders only at the edge of the charge-transfer band. The origin of this difference is not clear, but it could arise from other amine ligand conformations or coordination of oxidized cyclam ligand.

The UV/VIS spectrum of a mixture of complexes containing oxidized cyclam ligand in which one carbon–nitrogen double bond has been introduced shows band intensities to be much higher than for the saturated ligand systems. The spectrum is not of value for a configurational assignment, which has tentatively been made on the basis of the elution behaviour.

Conclusions. Attempts to reproduce the synthetic approach in Ref. 8 using methanol or other alcoholic solvents were not particularly successful. The major amount of starting material was invariably converted into iridium metal, and only minor amounts of complexes could be isolated. Purification using column chromatography as described in the experimental section gave compounds with the spectral characteristics given in Figs. 1 and 2.

The compound Ir(thtp)$_3$Cl$_3$ is a useful starting material for the preparation of isomerically pure trans-[Ir(cyclam)Cl$_2$]Cl in high yield. This method appears, however, to be critically dependent on the solubility characteristics of the product. Other amines were tested,

but only dark brown amine decomposition products were apparently formed.

Experimental

Caution! The perchlorate salts described here are potentially explosive and should be handled accordingly.

Materials. 1,4,8,11-tetraazacyclotetradecane (cyclam) was prepared according to the literature.[13] cis- and trans-[Cr(cyclam)Cl$_2$]Cl were prepared by a modified literature method.[2] The chloride salt of the trans isomer was converted into the trifluoromethanesulfonate salt by precipitating a saturated aqueous solution with 1 M CF$_3$SO$_3$Na, and recrystallizing the grayish green product from water at 80°C. The yield of trans-[Cr(cyclam)Cl$_2$]CF$_3$SO$_3$ is almost quantitative. Analyses, CrCl$_2$SF$_3$O$_3$N$_4$C$_{11}$H$_{24}$: Cr, C, H, N and Cl. All other chemicals were commercial products of analytical or reagent grade and were used without further purification.

Instrumentation. The purity of the products was controlled by FPLC chromatography using a Pharmacia FPLC apparatus equipped with a Mono S HR 5/5 column. Gradient elution from aqueous 0.01 M HBr to aqueous 0.01 M HBr + 0.20 M NaBr was used for the separations.

The absorption spectra were recorded on a Perkin-Elmer Lambda 17 spectrophotometer.

Proton-decoupled ^{13}C NMR spectra were recorded at 62.896 MHz with a Bruker AC 250 MHz Fourier-transform spectrometer. Data, typically about 3×10^4 transients, were recorded at 300 K using a pulse width of 2 μs (45°), sweep width 14200 Hz and 32 K data points, giving a digitizer resolution of 0.87 Hz/point in the final spectrum. Under these conditions the acquisition time is 1.147 s per free induction decay, and a relaxation delay between pulses was not found to be necessary. Chemical shifts are reported on the δ-scale with reference to solvent DMSO at $\delta = 39.5$ ppm.

X-Ray powder diffraction photographs were taken with a Hägg–Guinier focusing camera XDC 700 calibrated with silicon and using Cu $K\alpha$ radiation.

C, H, N, Cl and S analyses were performed by the Microanalytic Section of the Department of Chemistry at the University of Copenhagen.

Synthetic procedures.

(1) Ir(thtp)$_3$Cl$_3$. This compound was prepared by a method analogous to that for the preparation of Ir{(C$_2$H$_5$)$_2$S}$_3$Cl$_3$[14] with K$_2$IrCl$_6$ substituted for (NH$_4$)$_2$IrCl$_6$ and tetrahydrothiophene for diethyl sulfide. Yield: 75–86%. The crude product was used directly for preparation (3). It was not attempted to separate

the mixture of isomers such as [Ir(thtp)$_3$Cl$_3$] and [Ir(thtp)$_4$Cl$_2$][Ir(thtp)$_2$Cl$_4$].[15-17]

(2) trans-*[Ir(cyclam)Cl$_2$]Cl.* 1.00 g (1.78 mmol) of [Ir(thtp)$_3$Cl$_3$] and 0.40 g of cyclam (2.00 mmol) were added to 5 ml of DMSO. The suspension was heated with stirring to 145°C. After a few minutes a clear orange solution was formed and yellow crystals began to precipitate. Heating was continued for 2 h, after which the mixture was allowed to cool to room temperature. The crystals were filtered off, washed twice with 2 ml DMSO and then with diethyl ether, and dried in air. Yield: 0.50 g (56%) of crude trans-[Ir(cyclam)Cl$_2$]Cl.

The combined mother liquor and washings may be treated as described in preparations (3) and (4) to give about 0.05 g cis-[Ir(cyclam)Cl$_2$]Cl and minor amounts of impure trans-[Ir(imine–cyclam)Cl$_2$]ClO$_4$.

trans-[Ir(cyclam)Cl$_2$]Cl was recrystallized by dissolving 1.00 g in 10 ml of water by heating to boiling followed by filtration and addition of 8 ml of 2 M LiCl to the filtrate. The solution was allowed to stay for crystallization first at room temperature and then at 5°C overnight. The crystals were filtered off, washed twice with 2 ml of ice-cold water and dried in air. Yield: 0.85 g (85%) of trans-[Ir(cyclam)Cl$_2$]Cl. Analyses, IrCl$_3$N$_4$C$_{10}$H$_{24}$: C, H, N and Cl. ^{13}C NMR: δ/ppm = 31.2, 51.6 and 55.5 in D$_2$O + DMSO (1 : 1 vol/vol).

The compound crystallized with varying amounts of water, which was lost upon standing for a few days. The chloride salt could be transformed into the trifluoromethanesulfonate salt as described above for the analogous chromium(III) compound. The yield of trans-[Ir(cyclam)Cl$_2$]CF$_3$SO$_3$ was almost quantitative. Analyses, IrCl$_2$SF$_3$O$_3$N$_4$C$_{11}$H$_{24}$: C, H, N and Cl.

(3) cis-*[Ir(cyclam)Cl$_2$]Cl.* 2.00 g of IrCl$_3$·4H$_2$O (5.38 mmol) were refluxed in 75 ml of water for 30 min. The solution was evaporated to dryness, redissolved in 50 ml of water and then added to 1.10 g of cyclam (5.49 mmol) in a Teflon flask. The container was closed and placed in a steel autoclave containing water for pressure equilibration and heated to 150°C for 24 h. The resulting mixture was filtered in order to remove iridium metal. The orange filtrate was diluted to 200 ml with water and passed through a short column containing 2 g of SP-Sephadex C-25 in the Li$^+$ form. This treatment removed some brown polymeric material and gave a yellow solution of apparently monomeric species. Monomeric species still on the column were removed with 50 ml of 0.1 M LiCl, and the combined filtrate and eluate was evaporated to a volume of 20 ml. The dropwise addition of 5 ml of 70% HClO$_4$ gave a yellow precipitate and the mixture was left overnight at 5°C. The yellow crystals were filtered off, washed with 5 ml of water and then with 96% ethanol, and dried in air. Yield: 0.78 g of a crude [Ir(cyclam)Cl$_2$]ClO$_4$ mixture.

0.75 g of the crude product was dissolved in 200 ml of water and the solution was applied to a column, about 50 cm long and 2.5 cm in diameter, containing 40 g of SP-Sephadex C-25 in the Li$^+$ form. This gave a yellow band at the top of the column which could be separated into two bands by elution with 0.1 M LiCl. The first fraction was a broad band which contained trans isomers of oxidized cyclam ligand, *cf.* preparation (4). The second fraction, which contained cis-[Ir(cyclam)Cl$_2$]$^+$, was evaporated to dryness. Lithium chloride was removed by extraction with 96% ethanol, and the remaining crystals were filtered off, washed with 96% ethanol and dried in air. Yield: 0.25 g (9%) of cis-[Ir(cyclam)Cl$_2$]Cl.

cis-[Ir(cyclam)Cl$_2$]Cl was recrystallized by dissolving 1.00 g in 10 ml of water by heating to boiling followed by filtration. The filtrate was allowed to stay for crystallization first at room temperature and then overnight at 5°C. The crystals were isolated as described above. Yield: 0.70 g (70%) of cis-[Ir(cyclam)Cl$_2$]Cl. Analyses, IrCl$_3$N$_4$C$_{10}$H$_{24}$: C, H, N and Cl. ^{13}C NMR: δ/ppm = 23.1, 47.1, 49.5, 50.0 and 55.4 in DMSO.

(4) trans-*[Ir(imine-cyclam)Cl$_2$]ClO$_4$.* Fraction I from preparation (3) was evaporated to a volume of about 25 ml. The solution was filtered to remove minor amounts of unidentified material and 5 ml of 70% HClO$_4$ were added to the filtrate. The resulting solution was allowed to stand overnight at 5°C. The crystals were filtered off, washed with 5 ml of water and then with 96% ethanol, and dried in air. Yield: 0.20 g (7%) of impure trans-[Ir(imine–cyclam)Cl$_2$]ClO$_4$. Analyses, IrCl$_3$O$_4$N$_4$C$_{10}$H$_{22}$: C, H, N and Cl. This product could be recrystallized from the minimum amount of 1 M hydrochloric acid at 100°C by the addition of 1/10 volume of saturated NaClO$_4$ and cooling to room temperature.

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