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Thermal isomerization of *cis*-[Fe(cyclam)Cl_2]Cl·H_2O complex in the solid state

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Abstract

The solid state thermal isomerization of *cis*-[Fe(cyclam)Cl_2]Cl·H_2O (cyclam is 1,4,8,11-tetraazacyclotetradecane), is investigated by TG/DSC, electrochemical and vibrational spectroscopic methods. The thermal isomerization of this complex was found to be water dependent and endothermic. An aquation–anation pathway that precedes the macrocyclic ligand stereochemical rearrangement in the complex is proposed. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The chemistry of transition-metal complexes involving macrocyclic ligands such as cyclam (1,4,8,11-tetraazacyclotetradecane) has been of major interest in the fields of catalysis [1], photochemistry [2], chemical analysis [3] and pharmacology [4]. Recently, the cyclam derivative (bicyclam) and its Zn^{2+} complex have shown remarkable anti-HIV activity [4]. Also, the $[Ni(cyclam)]^{2+}$ complex has exhibited an important electrocatalytic property towards the conversion of CO_2 to methanol [1].

Studies on the iron–cyclam system are scarce as compared to those of the ruthenium–cyclam, ruthenium-bis(2,2′-bipyridine) and ruthenium-amine complexes [2,5,6]. The preparation of iron-amine derivative complexes is not possible due to iron hydrolysis side-reactions. The macrocyclic ligand, 1,4,8,11-tetraazacyclotetradecane, mimics some of the amine properties providing the metal complex stability gain due to its polydentate attributes [7]. Consequently, the study of iron–cyclam species is of interest to correlate with those of ruthenium and osmium amine derivative complexes with respect to properties and reactivity [5–10]. Although, examples of solid state linkage and diastereomeric isomerisms are common [11–14], there is no report concerning *cis–trans* isomerism for amine and 2,2′-bipyridine Ru and Os derivative complexes.

The $[Fe(cyclam)Cl_2]^+$ complex crystallizes in *cis* and *trans* configurations that present different physical and chemical properties, such as the reactivity towards oxygen [15]. The *cis*-to-*trans*-$[Fe(cyclam)Cl_2]^+$ conversion has been systematically investigated in solution to establish the synthetic route for the isomer

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preparations [15,16]. However, the yields obtained for the conversion are still considered low. We report here the results of the solid state thermal isomerization of the *cis*-$[Fe(cyclam)Cl_2]^+$ that can be used as a potential new synthetic route to the *trans*-$[Fe(cyclam)Cl_2]^+$ complex.

2. Experimental

2.1. Cis-$[Fe(cyclam)Cl_2]Cl\cdot H_2O$

A quantity of 280 mg (1.4 mmol) of $FeCl_2\cdot 4H_2O$ were dissolved in 20 ml of methanol and added to a 20 ml of degassed methanol solution containing 282 mg (1.4 mmol) of the cyclam ligand. Although, a dark green color immediately developed, the reaction was allowed to proceed during 3 h under argon flow at ambient temperature. The resulting solution was then exposed to air. The yellow *cis*-$[Fe(cyclam)Cl_2]Cl\cdot H_2O$ complex was collected by filtration, washed with cold methanol, dried and stored under vacuum. Yield was ~45%. The dark brown filtrate resulting from the *cis*-$[Fe(cyclam)Cl_2]Cl\cdot H_2O$ separation was further used in the synthesis of the *trans*-$[Fe(cyclam)Cl_2](BF_4)$. Elemental analysis: calc. for $C_{10}H_{26}N_4OCl_3Fe$: C, 31.5%; N, 14.7%; H, 6.8%. Found: C, 31.9%; N, 14.5%; H, 6.7%. CV: $E_{1/2} = 200$ mV versus Ag/AgCl. IR: N–H vibrations: 866, 858, 850 cm^{-1}; CH_2 vibrations: 808, 794 cm^{-1}.

2.2. Trans-$[Fe(cyclam)Cl_2](BF_4)$

The dark brown filtrate from the *cis*-$[Fe(cyclam)Cl_2]Cl\cdot H_2O$ preparation was refluxed for 1 h and then exposed to air at ambient temperature. The addition of 2 ml of a 45% aqueous solution of HBF_4 yields an yellow–greenish solid that was collected by filtration, washed with cold methanol, dried and stored under vacuum. Yield was ~30%. Elemental analysis: calc. for $C_{10}H_{24}N_4BF_4Cl_2Fe$: C, 30.0%; N, 13.5%; H, 5.8%. Found: C, 29.7%; N, 13.7%; H, 5.6%. CV: $E_{1/2} = 83$ mV versus Ag/AgCl. IR: N–H vibrations: 890, 888 cm^{-1}; CH_2 vibrations: 810 cm^{-1}.

2.3. Physical measurements

Thermoanalytical measurements were carried out with a Shimadzu DSC-50 and TGA-50. The experiments were performed under a nitrogen atmosphere (50 $cm^3\,min^{-1}$), heating rate of 10°C min^{-1} and 2–5 mg samples.

Electrochemical experiments were performed using a potentiostat model 100BW from Bioanalytical Systems (BAS) interfaced to an IBM PC/AT. Differential pulse voltammetry (DPV) of the *cis*- and *trans*-$[Fe(cyclam)Cl_2]X$ ($X = Cl^-$, BF_4^-) complexes and for the thermal residues were measured in KCl 1 mol l^{-1} as electrolyte, using a conventional three-electrode glass cell with a glass carbon of 0.614 cm^2 of geometrical area, Ag/AgCl–KCl 3, 5 mol l^{-1} and a Pt foil as working, reference and auxiliary electrodes, respectively.

Infrared spectra were recorded on a FT-IR Shimadzu 283-B spectrometer and samples were prepared as 1% dispersions in KBr pellets.

3. Results

Fig. 1 shows the TG and DSC curves of *cis*-$[Fe(cyclam)Cl_2]Cl\cdot H_2O$. The TG curve indicates two mass losses over the temperature range 20–400°C. The DSC curve shows that there are endothermic processes, and an additional sharp peak at 243°C is indicated.

The product obtained by heating the *cis*-$[Fe(cyclam)Cl_2]Cl\cdot H_2O$ at 243°C changed color from the original yellow to green before and after this peak. DPV of this residue showed the appearance of an additional peak, $E_{1/2} = 83$ mV versus Ag/AgCl, characteristic for the $Fe^{III/II}$ redox process of the *trans*-$[Fe(cyclam)Cl_2]Cl\cdot H_2O$ complex. The infrared spectrum of the same residue indicated the typical vibrational mode of the *trans*-$[Fe(cyclam)Cl_2]Cl\cdot H_2O$ complex at 890 cm^{-1}.

To further characterize the thermal residues, the *cis*-$[Fe(cyclam)Cl_2]Cl\cdot H_2O$ complex was heated isothermally at 214°C (yellow product), and 243°C (green product), for 20 min, and analyzed by DPV. The DPV curve for the yellow product presented a unique redox process ($E_{1/2} = 200$ mV) characteristic of the *cis*-$[Fe(cyclam)Cl_2]^+$. For the green product, an additional peak appears with $E_{1/2} = 83$ mV, typical of the redox process of the *trans*-$[Fe(cyclam)Cl_2]^+$ complex.

Upon heating the sample up to 250°C the DSC curve performed for the sample cooling to ambient

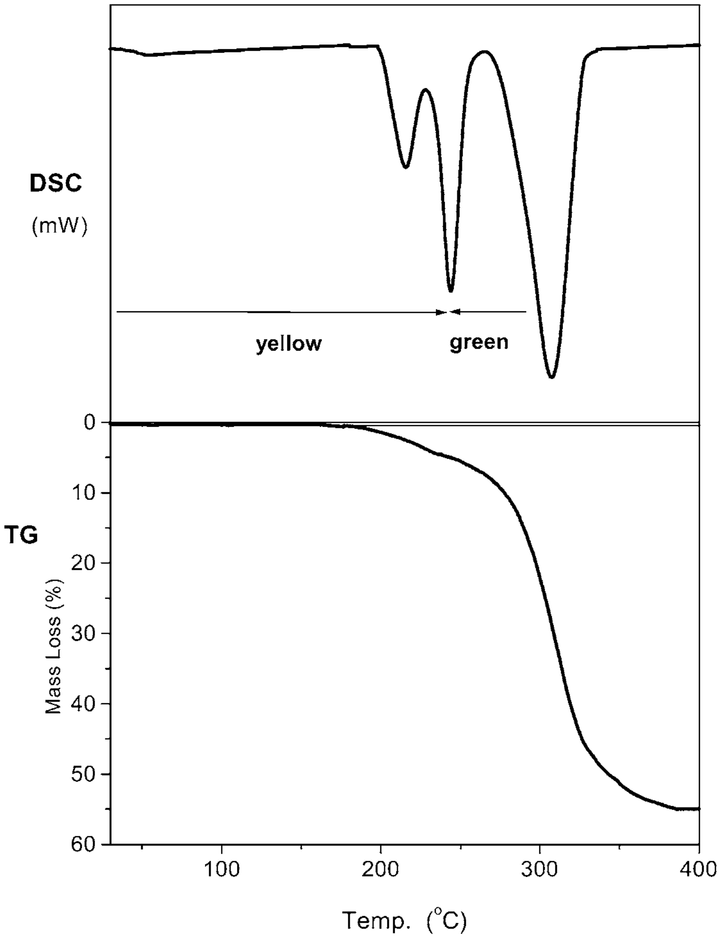

Fig. 1. TG and DSC curves of *cis*-[Fe(cyclam)Cl_2]Cl·H_2O complex.

temperature show no peak that would characterize the *trans*-to-*cis* isomerization. This result suggests that the thermal isomerization *cis*-to-*trans*-[Fe(cyclam)Cl_2]Cl is non-reversible, as observed for other tetraazacycloalkane complexes [17].

4. Discussion

The TG curve of the *cis*-[Fe(cyclam)Cl_2]Cl·H_2O complex shows a mass loss at 175–230°C, which corresponds to 1 mol of lattice water (found, 4.9%; calcd., 4.7%). No further change in the TG curve was observed until the complex decomposed at about 306°C, with a mass loss corresponding to the 1 mol of coordinated cyclam (found, 51%; calcd., 52%). This assignment was supported by the electrochemical results. The DPV curve for the residue of the first mass loss show a typical electrochemical behavior of the *cis*-[Fe(cyclam)Cl_2]$^+$ complex ($E_{1/2} = 200$ mV versus Ag/AgCl). Furthermore, an intense endothermic DSC peak appears with no mass loss at 243°C, when the complex color was observed to change from yellow to green. The DPV curve for the green product showed an additional peak ($E_{1/2} = 83$ mV) identical to the $Fe^{III/II}$ redox potential of the *trans*-[Fe(cyclam)Cl_2]$^+$ complex, suggesting that this process is due to *cis*-to-*trans* isomerization. The infrared spectrum of this green product further supported the isomerization process by the appearance of a peak at

890 cm^{-1}, assigned to the CH_2 vibration mode of the *trans*-[Fe(cyclam)Cl_2]$^+$ complex [16].

On cooling the green product from 250°C to ambient temperature, the DSC curve show no peak that would characterize the *trans*-to-*cis* reversed process. Also, the green sample color which is characteristic of the *trans* isomer was kept unchanged. These observations indicate the irreversibility of the *cis*-to-*trans* isomerization thermal process in the solid state, similar to that observed for analogous systems described in the literature [17].

The formation of the *cis*-[Fe(cyclam)Cl_2]$^+$ complex in solution is first favored by the kinetic pathways that can be explained by conformational and steric effects [18]. Conformational changes in the macrocycle can arise subsequent to metal ion incorporation. The binding of the metal ion to a macrocycle is thought to easily occur first by the replacement of an axial solvent molecule followed by a Jahn–Teller inversion, which brings the coordinated macrocycle nitrogen donor atom into axial position. The other bond formations follows the similar pattern, being the *cis*-complex formation kinetically favored compared to the *trans* isomer. Such selectivity in the formation of the *cis*-tetraaza macrocycle isomer complex is in accordance with the so-called ring effects [19,20]. The best-fit M–N bond length calculated by Martin et al. [20] for the 14-aneN_4 tetraaza macrocycle, where the metal ions were constrained to be square planar, is 2.07 Å. This bond length value is shorter than the strain-free Fe–N distance (2.17 Å), making difficult the incorporation of Fe^{III} ion into small ligand holes in a coplanar geometry. These arguments well support the preferential formation of the *cis*-[Fe(cyclam)Cl_2]$^+$ complex from the synthesis procedure in solution.

The literature reports that *cis*-to-*trans* isomerization of metal complexes that proceed with participation of water occurs invariably by an endothermic pathway. Contrary, the geometrical configurational conversions that take place without water participation are essentially exothermic [17]. Therefore, the endothermic peak observed on the DSC curve for the *cis*-to-*trans*-[Fe(cyclam)Cl_2]Cl·H_2O isomerization (Fig. 1) indicates the water participation in this process.

In a previous study in solution, we have not observed any evidence of *cis*-to-*trans*-[Fe(cyclam)Cl_2]$^+$

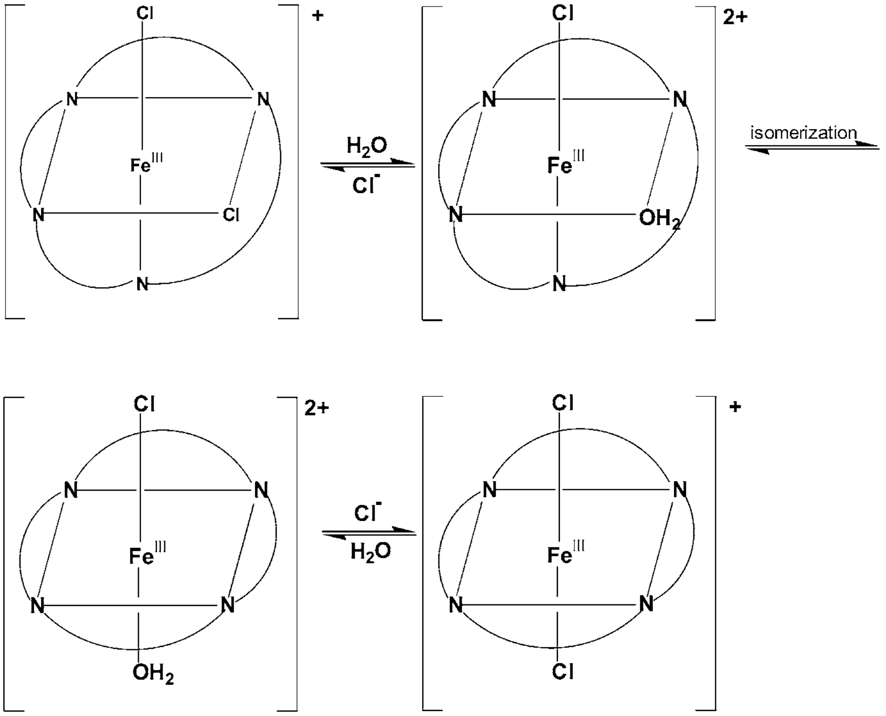

Fig. 2. Proposed mechanism for solid state *cis*-to-*trans*-[Fe(cyclam)Cl_2]Cl·H_2O isomerization.

isomerization in aprotic solvents, at least at the time scale of the experiment (methanol; 24 h). Conversely, the *cis*-to-*trans*-[Fe(cyclam)Cl_2]$^+$ isomerization takes place rapidly in water. The lack of isomerization in the absence of water would suggest that this molecule plays an important energetic role for the conversion.

These results along with the observations for the solid state reaction well support that the stereochemical changes involve an aquation–anation pathway. The aquation could result from high effective concentration of water in lattice due to its high mobility relative to charged species.

On the basis of these observations the mechanism for solid state *cis*-to-*trans*-[Fe(cyclam)Cl_2]Cl·H_2O isomerization is proposed in Fig. 2.

The mechanism involves an aquation–anation pathway mediated by the macrocyclic ligand stereochemical rearrangement in the complex. The solid state thermal isomerization of the *cis*-[Fe(cyclam)Cl_2]$^+$ complex constitutes a potential new synthetic route for the *trans*-[Fe(cyclam)Cl_2]$^+$ species.

Acknowledgements

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