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Solid phase thermal cis–trans isomerization of the bis(diamine) and tetraazacycloalkane complexes of the type $[(Co\ or\ Cr)X_2\{(diamine)_2\ or\ (mac)\}]^+$. Isomerization of *cis*-$[CoCl_2(cyclam)](Cl\ or\ BF_4)$ in the solid state

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Abstract

The solid phase thermal isomerization of *cis*-$[CoCl_2(cyclam)]$ (Cl or BF_4) was investigated by means of TG, DTA and DSC methods; cyclam is 1,4,8,11-tetraazacyclotetradecane. The complex was found to isomerize exothermically to the corresponding transform. Details of the isomerization of the complex were discussed along with the results previously obtained for $[(Co\ or\ Cr)X_2\{(aa\ or\ bb)_2,\ (aa)(bb)\ or\ (mac)\}]X \cdot nH_2O$, where X is Cl^-, Br^-, or BF_4^-; aa and bb are different diamines selected from 1,2-ethanediamine (en), *d,l*-1,2-propanediamine (pn), 1,3-propanediamine (tn), *d,l*-2,3-butanediamine (bn), *d,l*-1,2-cyclohexanediamine (chxn), or *d,l*-2,4-pentanediamine (ptn); and mac is cyclam, 1,4,7,11-tetraazacyclotetradecane (isocyclam), 1,4,8,12-tetraazacyclopentadecane ($[15]aneN_4$) or 1,5,9,13-tetraazacyclohexadecane ($[16]aneN_4$).

INTRODUCTION

We have serially investigated the details of the cis–trans isomerization of the cobalt(III) and chromium(III) complexes with the general formula $[(Co\ or\ Cr)X_2\{(aa\ or\ bb)_2,\ (aa)(bb)\ or\ (mac)\}]X \cdot nH_2O$ as illustrated in Fig. 1, where X is Cl^-, Br^- or BF_4^-; aa and bb are different diamines selected from 1,2-ethanediamine (en), *d,l*-1,2-propanediamine (pn), 1,3-propanediamine (tn), *d,l*-2,3-butanediamine (bn), *d,l*-1,2-cyclohexanediamine (chxn), or *d,l*-2,4-pentanediamine (ptn); and mac is 1,4,8,12-tetraazacyclopentadecane ($[15]aneN_4$) or 1,5,9,13-tetraazacyclohexadecane ($[16]aneN_4$) [1–9]. Figure 2 shows the framework and abbreviations of the

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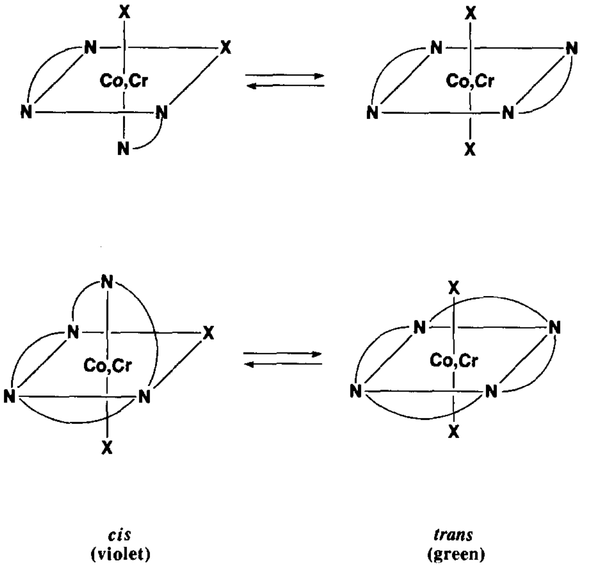


Fig. 1. The cis–trans isomerization of the bis(diamine) and tetraazacycloalkane cobalt(III) and chromium(III) complexes. N–N and N–N–N–N are diamines (aa or bb) and tetraazacycloalkanes (mac) illustrated in Fig. 2, respectively; X is Cl^- or Br^-.

diamines (aa or bb) and tetraazacycloalkanes (mac) used in the present study.

Trans-to-cis isomerization was detected in the simple bis(diamine) complexes [(Co or Cr)X_2(aa)$_2$]X [10] containing en [1], pn [2], bn [3] and chxn [4], which are capable of forming a 5-membered chelate ring with metal ions, whereas cis-to-trans isomerization was recognized in the complexes containing tn [5] and ptn [4], which form a 6-membered chelate ring. In the case of the mixed bis(diamine) complexes [(Co or Cr)X_2(aa)(bb)]X [10], only trans-to-cis isomerization was found even when the complexes contained both 5- and 6-membered chelate rings [4–7].

The essential difference in the solid-phase isomerization between the cobalt(III) and chromium(III) complexes was that the isomerization of the cobalt(III) complexes takes place endothermically along with the dehydration of lattice water, whereas the isomerization of the chromium(III) complexes is in all cases exothermic and does not require the participation of lattice water. Thus, we tentatively proposed that an intermolecular aquation–anation mechanism is favorable for the isomerization of the cobalt(III) complexes, and an intramolecular bond-rupture mechanism is predominant for the chromium(III) complexes.

In addition, we recently discovered the interesting fact that the *cis* chromium(III) complexes containing a mac such as [15]aneN_4 or [16]aneN_4 isomerize exothermically with no participation of water, al-

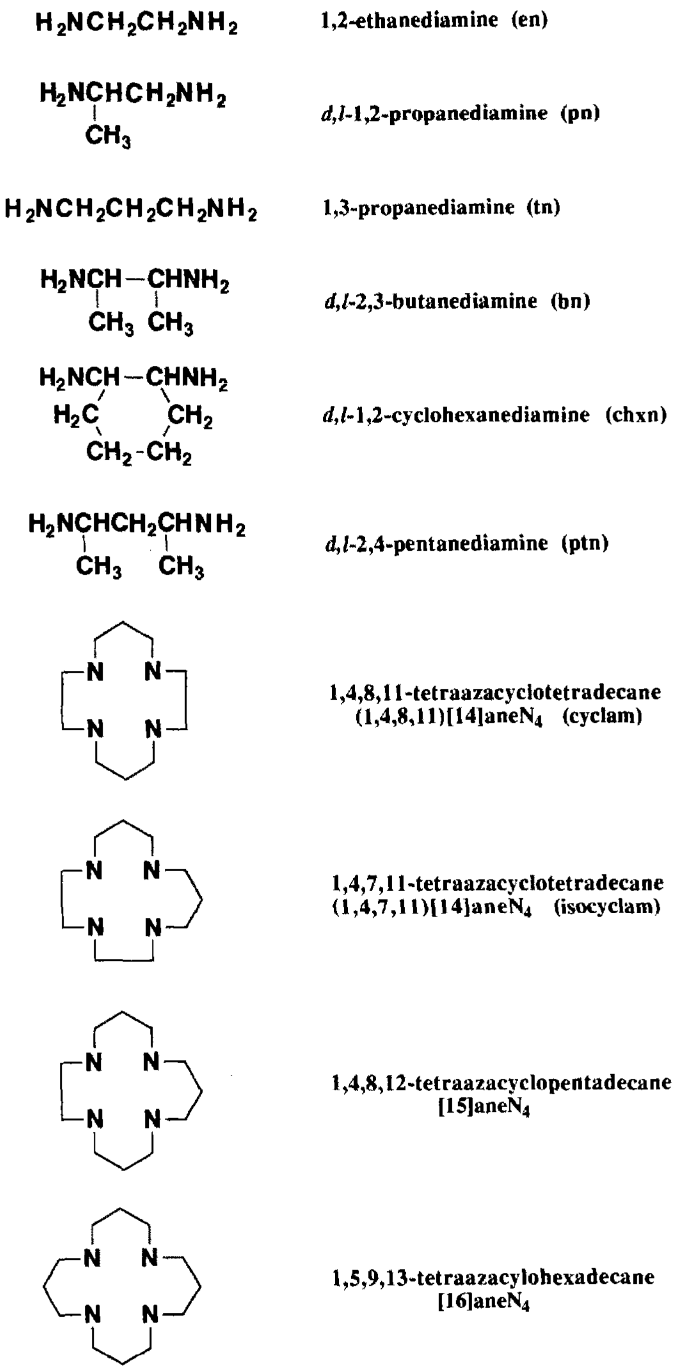


Fig. 2. Framework and abbreviations of diamines (aa or bb) and tetraazacycloalkanes (mac) in the present work.

though we had at first speculated that the complexes would never isomerize in the solid state because the mac compounds ([15]aneN_4 and [16]aneN_4) have rigid ring structures obtained by fusing together en and tn. Then it is necessary to establish whether or not the participation of water is required for the isomerization of the tetraazacycloalkane cobalt(III) complexes.

Work was therefore undertaken to investigate the solid state isomerization of the cobalt(III) complexes containing 1,4,8,11-tetraazacyclotetradecane (cyclam), 1,4,7,11-tetraazacyclotetradecane (isocyclam) and [15]aneN_4. The cyclam complexes were found to isomerize from cis to trans with no participation of water. The isomerization of the complexes was also considered in connection with the results obtained previously.

EXPERIMENTAL

Preparation of ligands and complexes

Cyclam [11], isocyclam [12] and [15]aneN_4 [13] were prepared by the same methods as those described in literature. The *cis*- [14] and *trans*-[$CoCl_2$(cyclam)]Cl [15] complexes were prepared according to published procedures, and *cis*- and *trans*-[$CoCl_2$(cyclam)]BF_4 were obtained by metathesis of the corresponding chlorides with $NaBF_4$.

Analysis: found for *cis*-[$CoCl_2$(cyclam)]Cl: C, 32.85; H, 6.57; N, 15.32%. Found for *trans*-[$CoCl_2$(cyclam)]Cl: C, 32.73; H, 6.67; N, 15.25%. Calcd. for $C_{10}H_{24}N_4Cl_3Co$: C, 32.85; H, 6.62; H, 15.32%.

Analysis: found for *cis*-[$CoCl_2$(cyclam)]BF_4: C, 28.93; H, 5.87; N, 13.47%. Found for *trans*-[$CoCl_2$(cyclam)]BF_4: C, 28.86; H, 5.80; N, 13.59%. Calcd. for $C_{10}H_{24}N_4Cl_2CoBF_4$: C, 28.81; H, 5.80; N, 13.44%.

Attempts to prepare *cis*-[$CoCl_2$(isocyclam)]Cl and *cis*-[$CoCl_2$-([15]ane-N_4)]Cl failed because a mixture of the cis and trans forms was always obtained for isocyclam, and only the trans complex for [15]aneN_4.

Measurements

Visible and ultraviolet absorption spectra were measured in dimethyl sulfoxide (DMSO) and methanol with a Hitachi U-3500 spectrophotometer. IR spectra were measured with a Jasco Model A-3 infrared spectrophotometer. TG, DTA and DSC measurements were carried out with a Seiko TA Station SSC 5000 system under a nitrogen stream (100 $cm^3\,min^{-1}$), 10–20 mg of finely powdered sample being used. The heating rate was 1.0°C min^{-1}. The heating processes were also observed by using a Chyo 100-L thermobalance.

RESULTS

Figure 3 shows the TG, DTA and DSC curves of *cis*-[$CoCl_2$(cyclam)]Cl and *cis*-[$CoCl_2$(cyclam)]BF_4. As seen from the figure, the TG curves of both the chloride and the tetrafluoroborate remain unchanged until the compounds decompose rapidly at about 230°C. On the other hand, the DTA curves of both the complexes have two humped exothermic peaks at 179 and 194°C for the chloride and at 160 and 171°C for the tetrafluoroborate. Similar situations can be seen on the DSC curves. The complexes changed color from the original violet to green before and after the humped peaks. Figure 4 shows the electronic spectra of *cis*- and *trans*-[$CoCl_2$(cyclam)]Cl and the product obtained by heating the cis complex at 160°C for 1 h. The spectrum of the product closely resembles that of the trans complex, indicating that the above humped DTA and DSC curves are due to cis-to-trans isomerization of the cis complexes.

Occurrence of the two humped DTA and DSC peaks may imply that two processes are involved at very close temperatures in the isomerization. Unfortunately we were not able to differentiate the two processes because we could not isolate any intermediate during the isomerization, except that a mixture of the cis and trans forms was always obtained. Thus, the reason that two humped exothermic DTA and DSC peaks

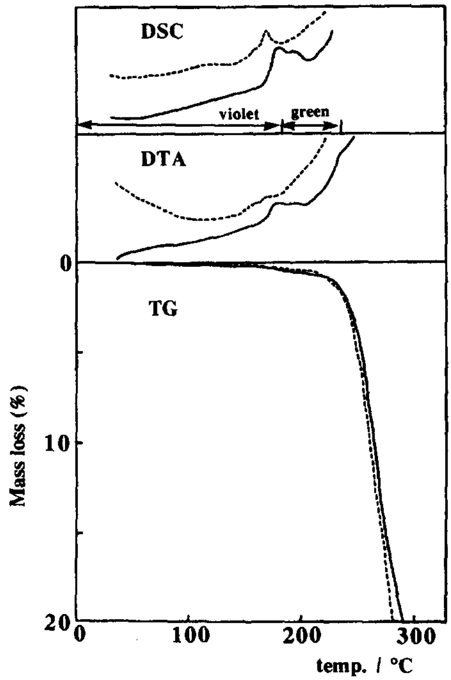


Fig. 3. TG, DTA and DSC curves of *cis*-[$CoCl_2$(cyclam)]Cl (———) and *cis*-[$CoCl_2$(cyclam)]BF_4 (------).

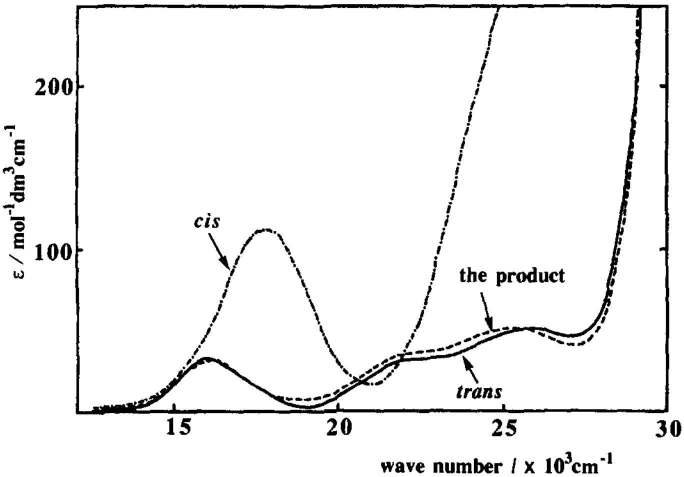


Fig. 4. Electronic spectra of *cis*-[$CoCl_2$(cyclam)]Cl (- · -), *trans*-[$CoCl_2$(cyclam)]Cl (———), and the product obtained by heating the cis complex at 160°C for 1 h (------). The solvents are DMSO for the cis complex and methanol for the trans complex and the product, respectively.

appear is still not clear, but a plausible idea might be that the complexes *cis*-[CoClCl*(cyclam)]X ($X = Cl, BF_4$) are first converted into transient *cis*-[CoClX(cyclam)]Cl* and then *trans*-[CoClCl*(cyclam)]X; the former reaction process takes place at a temperature very close to that of the latter process. The idea might be supported by the fact that violet *cis*-[$CrCl_2$([15]aneN_4)]SCN is exothermically converted into, first, red *cis*-[CrCl(NCS)([15]aneN_4)]Cl at 200°C and then green *trans*-[$CrCl_2$([15]aneN_4)]SCN at 250°C [9].

DISCUSSION

Participation of water in isomerization

Figure 5 illustrates the temperature ranges for dehydration and/or dehydrohalogenation and for isomerization of the simple and mixed bis(diamine) complexes and the tetraazacycloalkane complexes. Inspection of the figure tells us that the isomerization of the bis(diamine) cobalt(III) complexes takes place along with dehydration and dehydrohalogenation (*trans*-[$CoCl_2(pn)_2$]Cl · HCl · $2H_2O$ and *trans*-[$CoCl_2(pn)_2$]Cl · HCl · $2H_2O$), and along with dehydration and evolution of DMSO (*cis*-[$CoCl_2(tn)_2$]Cl · DMSO · $2H_2O$). In contrast, the isomerization of the bis(diamine) chromium(III) complexes takes place independent of dehydration and/or dehydrohalogenation. The same situation is also true for the tetraazacycloalkane chromium(III) complex (*cis*-$CrCl_2$([15]aneN_4)]Cl · H_2O). As described in the Results section, the

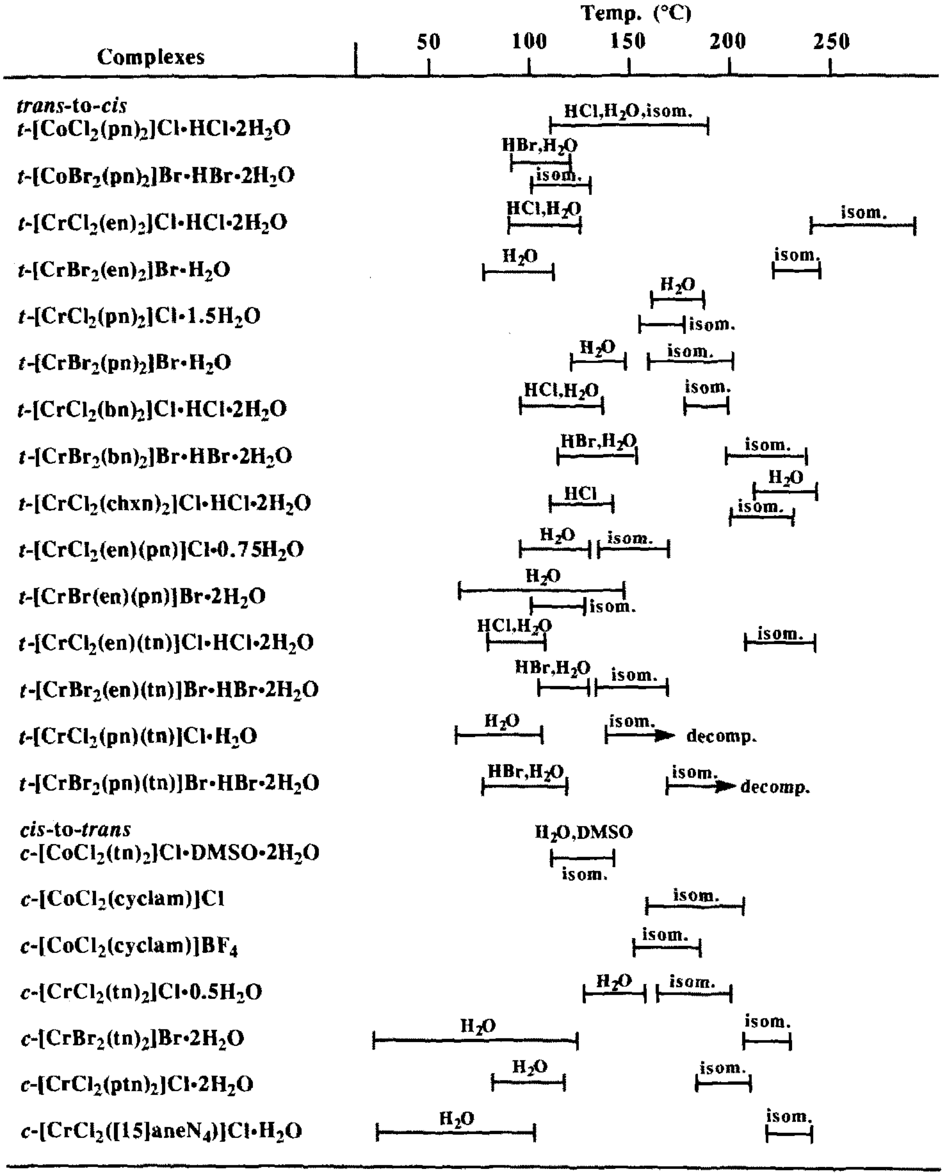


Fig. 5. Temperature ranges for dehydration and/or dehydrohalogenation and for isomerization of the simple and mixed bis(diamine) complexes and the tetraazacycloalkane complexes. HCl,H_2O: dehydrochlorination and dehydration; isom: isomerization; HBr,H_2O: dehydrobromination and dehydration; H_2O: dehydration; HCl: dehydrochlorination; H_2O,DMSO: dehydration and evolution of DMSO.

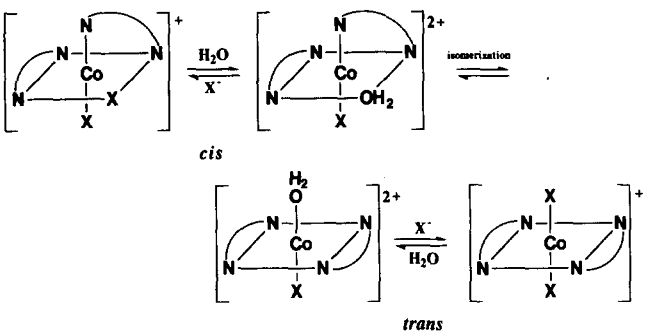
cyclam cobalt(III) complex *cis*-[$CoCl_2$(cyclam)] (Cl or BF_4) isomerized even with no lattice water.

Direction of isomerization

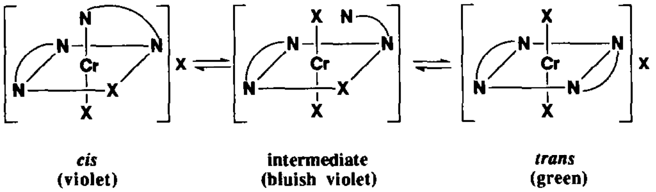
As seen from Fig. 5, the simple bis(diamine) complexes having two five-membered chelate rings isomerize from trans to cis irrespective whether they are cobalt(III) or chromium(III) complexes (the en, pn, bn, and chxn complexes). On the other hand, cis-to-trans isomerization was recognized for the simple bis(diamine) complexes containing two six-membered chelate rings (the tn and ptn complexes). We at first expected that the mixed bis(diamine) complexes having a combination of 5- and 6-membered chelate rings (the (en)(tn) and (pn)(tn) complexes) would undergo both cis-to-trans and trans-to-cis isomerizations. However, the expectation was not fulfilled: the isomerization was one way (trans-to-cis). The isomerization of the tetraazacycloalkane (cyclam and [15]aneN_4) complexes was cis-to-trans.

Proposed isomerization pathways

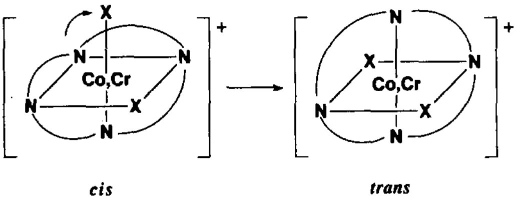
Figure 6 represents the proposed isomerization pathways of the bis(diamine) and the tetraazacycloalkane complexes. As mentioned in the Results section, *cis*-[$CoCl_2$(cyclam)] (Cl or BF_4) was unexpectedly found to isomerize with no participation of water. Previously [1–9] we have invariably detected that the isomerization of the cobalt(III) complexes takes place endothermically with the participation of water, whereas the chromium(III) complexes isomerize exothermically with no participation of water. For a feasible explanation of the above contrasting results, we propose the following isomerization pathways: in the case of the bis(diamine) cobalt(III) complexes, an aquation–anation pathway (Fig. 6(A)) [16] is predominant in which lattice water is involved in the isomerization. In contrast, a bond rupture pathway (Fig. 6(B)) is favorable for the bis(diamine) chromium(III) complexes, in which one of diamines in the intermediate is coordinated as unidentate toward chromium(III) ion. The idea receives support from the fact that *mer*-[$CrCl_3(bn)_2$] · H_2O [3], *mer*-[$CrBr_3$(en)(pn)] · $2H_2O$ [4] and *mer*-[$CrBr_3$(pn)(tn)] · $2H_2O$ [4, 6], where one of diamines acts as a monodentate ligand, were isolated as the intermediates in the isomerizaion of *trans*-[$CrCl_2(bn)_2$]Cl · HCl · $2H_2O$, *trans*-[$CrBr_2$(en)(pn)]Br · $2H_2O$ and *trans*-[$CrBr_2$(pn)(tn)]Br · HBr · $2H_2O$, respectively. Although the isomerization of the tetraazacycloalkane (mac) complexes cannot be fully understood, the fact that *cis*-[$CoCl_2$(cyclam)](Cl or BF_4) and *cis*-[$CrCl_2$([15]aneN_4)]Cl · H_2O isomerize with no participation of water implies that at least one of the four nitrogen atoms in the mac moves from one coordination site to another as shown in Fig. 6(C).



(A) aquation-anation



(B) bond-rupture



(C) Movement of tetraazacycloalkane (mac)

Fig. 6. Proposed isomerization pathways of the bis(diamine) and the tetraazacycloalkane complexes.

On the basis of the above results, we can conclude that any coordinated ligand in the metal complexes is unexpectedly easy to move, even in the solid state.

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