CROATICA CHEMICA ACTA CCACAA **74** (3) 499–528 (2001)

ISSN-0011-1643
CCA-2747 *Review*

Linkage Isomerization Reactions*

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Received August 28, 2000; revised February 19, 2001; accepted February 23, 2001

Linkage isomerization reactions have been reviewed from the aspect of the kinetics and mechanisms involved, focusing on selected cases of direct formation, as well as on electrochemical, photochemical, thermal and pH-induced generation of linkage isomers.

Key words: linkage isomerism, reaction mechanism, kinetics.

INTRODUCTION

Linkage isomerism has been classified as a particular phenomenon associated with metal complexes containing ambidentate ligands, *i.e.*, with at least two different donor atoms or binding sites. In this context, it is important to keep the same denticity and geometric configuration, so that the coordination of such ligands to the metal ion can only involve different combinations of donor atoms, leading to the corresponding isomers. These are now referred to by the Greek letter »κ« (kappa) preceding the binding atom.[1] This type of isomerism was first recognized by Alfred Werner in his classical report on the *xantho* and *isoxantho* forms of the $[(NH_3)_5Co(NO_2)]Cl_2$ complex.[2,3] The *xantho* complex corresponds to the more stable κ*N*, or nitro isomer, whereas the *isoxantho* complex corresponds to the κ*O* or nitrito isomer.[4,5] Since then, this system has been extensively investigated in solid state and in solution, constituting even at the present time the preferred study case in coordination chemistry courses.[6–9]

Ambidentate ligands can vary widely, from simple diatomic species such as the cyanide ion, to poly-N-heterocyclic bases, polynucleotides and pro-

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* Dedicated to Professor Smiljko Ašperger on the occasion of his 80th birthday.

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teins. In general, linkage isomerism has been discussed starting from the fact that the ligand binding atoms do not exhibit the same affinity for a particular metal center, thus supporting the thermodynamic considerations on the formation of coordination compounds. In a broad sense, however, practically all polyatomic ligands can give rise to linkage isomers, since even on the time scale of collision events many aleatory combinations are possible, generating transient isomeric species. The detection of such species, before their rearrangement or conversion into the thermodynamically stable ones, is a challenging kinetic problem which can be relevant in catalysis, because most of the reactive states are generated far from the thermodynamic equilibrium conditions. Therefore, the study of linkage isomerism can be extended by applying a dynamic approach, exploiting the lifetime of the several possible isomeric products or intermediate species. As a matter of fact, the most interesting cases of linkage isomerism have been associated with the generation of metastable isomers, such as the *isoxantho* complex, which are sufficiently long lived to allow monitoring of their conversion into the thermodynamically stable species.

Production of metastable linkage isomers depends on the intrinsic labile/inert characteristics of the metal complex, in addition to the metal-ligand affinities and stereochemical factors. For instance, metal complexes, exhibiting low spin d^5 and d^6 configurations are substitution inert. Although this aspect does not facilitate direct formation of metastable linkage isomers, most of the literature examples focuse on such substitutionally inert complexes, for practical reasons, since once they are generated, they can be easily monitored using conventional techniques.[3,10–18]

In fact, the procedures employed for generating metastable linkage isomers, seldom rely on direct methods, although this can not be excluded. Indirect synthetic methods are preferred, involving the formation of intermediate species that react or decompose, yielding metastable isomeric products. This is the case of the *xantho* and *isoxantho* isomers. The reaction of the $[Co(NH_3)_5(H_2O)]^{3+}$ complex with NO_2^- ions leads to the κ*N* isomer, while the formation of the κ*O* isomer proceeds *via* the reaction of the $[Co(NH_3)_5(OH)]^{2+}$ complex with the N_2O_3 species generated in HNO_2 solutions. Alternatively, metastable linkage isomers can be conveniently generated by means of photochemical,[19–38] thermal[24,38–49] or electrochemical methods.[49–72] In addition, examples of proton[36,46,52,53,58,73–77] or solvent-induced[47,76, 78–87] linkage isomerism are known.

Although a comprehensive survey of the literature is listed in the reference section, the full coverage of every example of linkage isomerism is an overwhelming task, far beyond the scope of this review article. Instead, we will focus our attention on selected examples of linkage isomerization reactions, exclud-

ing the classical NO_2^-,[9,22,27,31,33,34,40,47,49,57,59,83,88–120] SCN^-,[11,13,41,61,86,94,121–163] CN^-,[42,45,48,62–66,164–178] and related systems, with special emphasis on the kinetics and mechanistics involved.

DIRECT FORMATION OF LINKAGE ISOMERS

Linkage isomers can be produced in a typical dissociative substitution reaction carried out in the presence of ambidentate ligands, through their direct binding to the coordinatively unsaturated intermediate species. Perhaps the best example of a system reacting by a dissociative mechanism is given by the substituted pentacyanoferrate(II) complexes, $[Fe(CN)_5L]^{n-}$. This type of complex exhibits a $3d^6$ low spin configuration, with a pseudo-octahedral arrangement where the five cyanide ligands are strongly bound to the iron(II) center, and the sixth ligand L is more susceptible to substitution reactions in aqueous solution. Substitution kinetics in this complex type have been extensively investigated for a great variety of ligands L, using a number of techniques and experimental conditions.[179–201]

A typical feature is that the rates of substitution of ligand L in these complexes exhibit a saturation behavior with respect to the concentration of the entering ligands A, in agreement with the following mechanism:

$$[Fe(CN)_5L]^{3-} \rightleftharpoons [Fe(CN)_5]^{3-} + L \qquad (k_L,\ k_{-L}) \tag{1}$$

$$[Fe(CN)_5]^{3-} + H_2O \rightleftharpoons [Fe(CN)_5(H_2O)]^{3-} \tag{2}$$

$$[Fe(CN)_5]^{3-} + A \rightleftharpoons [Fe(CN)_5A]^{3-} \qquad (k_A,\ k_{-A}) \tag{3}$$

where

$$-d[\{Fe(CN)_5L\}]/dt = d[\{Fe(CN)_5A\}]/dt = k_{obsd}\ [\{Fe(CN)_5L\}] \tag{4}$$

and

$$k_{obsd} = (k_{-L}k_A[A] + k_{-A}k_L[L]) / (k_A[A] + k_L[L]) \tag{5}$$

According to Eq. (5), as [A] becomes sufficiently high, k_{obsd} tends to k_{-L}, which is the rate of dissociation of ligand L from the complex, measured at the saturation point. Another important aspect is that k_{-L} is independent of the nature of the attacking ligand A, the same applying to the activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$. In addition, a strong support for the dissociative

mechanism has also been obtained from the measurements of activation volumes. The reported values, in the range of 14–18 $cm^3\ mol^{-1}$ for L = H_2O,[179] and 20–21 $cm^3\ mol^{-1}$ for L = substituted pyridines,[189] are consistent with the expansion of the coordination shell up to the dissociation of the coordinated ligand in the activated complex.

Because of the dissociative mechanism involved, formation of the $[Fe(CN)_5]^{3-}$ intermediate species can be conveniently exploited in the generation of linkage isomers in the presence of ambidentate ligands, such as aminopyrazine and aminoacids. Using the X and Y designations for linkage isomers, the substitution process starting from the $[Fe(CN)_5(H_2O)]^{3-}$ complex involves two parallel reactions:

$$[Fe(CN)_5(H_2O)]^{3-} + XY \rightarrow [Fe(CN)_5(XY)]^{3-} + H_2O \qquad (k_X) \qquad (6)$$

$$[Fe(CN)_5(H_2O)]^{3-} + YX \rightarrow [Fe(CN)_5(YX)]^{3-} + H_2O \qquad (k_Y) \qquad (7)$$

where

$$k_{obsd}{}^{f} = (k_X + k_Y)\,[XY] \qquad (8)$$

Isomer X, which is more labile, isomerizes to the thermodynamically stable Y form, according to the dissociative scheme:

$$[Fe(CN)_5(XY)]^{3-} + H_2O \rightleftharpoons [Fe(CN)_5(H_2O)]^{3-} + XY \qquad (k_{-X},\ k_X) \qquad (9)$$

$$[Fe(CN)_5(H_2O)]^{3-} + YX \rightarrow [Fe(CN)_5(YX)]^{3-} \qquad (k_Y) \qquad (10)$$

Linkage isomerization proceeds according to a pseudo-first order kinetics, where the observed rate constant, $k_{obsd}{}^{isom}$, is independent of the concentration of the XY ligand, *i.e.*:

$$k_{obsd}{}^{isom} = (k_Y\ k_{-X}) / (k_X + k_Y) \qquad (11)$$

An important strategy for evaluating the kinetic constants involved in the isomerization scheme is adopted by introducing a competing ligand, A, such as dimethyl sulfoxide (dmso), which forms a very stable and inert complex with the pentacyanoferrate(II) ion. According to the competitive scheme, in addition to the parallel reactions expressed by k_X and k_Y, one should include:

$$[Fe(CN)_5(H_2O)]^{3-} + A \rightarrow [Fe(CN)_5A]^{3-} + H_2O \qquad (k_A) \qquad (12)$$

In this case, the observed rate constant for the substitution reaction in the starting $[Fe(CN)_5(H_2O)]^{3-}$ complex becomes

$$k_{obsd}{}^{f} = (k_X + k_Y)\,[XY] + k_A\,[A] \qquad (13)$$

From the slope and intercept of the linear plot of $k_{obsd}{}^{f}$ *versus* [A], at [XY] = constant (in excess), one can evaluate k_A and $(k_X + k_Y)$, respectively.

For the isomerization process, in the presence of A,

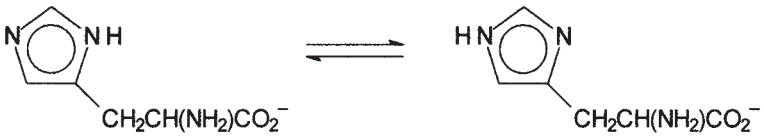
$$k_{obsd}{}^{isom} = \{k_{-X}(k_Y[XY] + k_A[A]\} \,/\, \{(k_X + k_Y)[X{-}Y] + k_A[A]\} \qquad (14)$$

Therefore,

$$k_{obsd}{}^{f} \times k_{obsd}{}^{isom} = k_{-X}\,(k_Y\,[XY] + k_A\,[A]) \qquad (15)$$

The product of $k_{obsd}{}^{f}$ and $k_{obsd}{}^{isom}$ corresponds to a linear equation *versus* [A] (Eq. 15), which yields $k_A \cdot k_{-X}$ and $k_Y \cdot k_{-X}$ from the slope and intercept, respectively. Since k_A has already been determined (from Eq. 13), k_{-X}, k_Y and k_X can be calculated.

This approach has been successfully employed[202] to obtain the linkage isomerization kinetic parameters in pentacyanoferrate(II) complexes with aminoacids. An interesting case is the investigation of the tautomerism of histidine in aqueous solution.[203] Histidine is an essential aminoacid that, in the zwitterionic form, exhibits a tautomeric equilibrium,



(16)

or

$$\text{N(1)-his} \rightleftharpoons \text{N(3)-his} \qquad (17)$$

Both the N(1) and N(3) nitrogens of the imidazole ring are available for coordination; however, the N(3) tautomer should yield a less stable complex due to steric effects. In spite of this, kinetics has shown that this isomer is formed preferentially.

$$[Fe(CN)_5(H_2O)]^{3-} + N(3)\text{-his} \rightarrow [Fe(CN)_5\{N(3)\text{-His}\}]^{3-} + H_2O \quad (18)$$

$$[Fe(CN)_5(H_2O)]^{3-} + N(1)\text{-his} \rightarrow [Fe(CN)_5\{N(1)\text{-His}\}]^{3-} + H_2O \quad (19)$$

Although both isomeric forms exhibit very similar electronic spectra, they can be discriminated kinetically, for their contrasting reactivity in the presence of dmso. By solving the two-step kinetics, all the associated constants have been obtained, as summarized in Table I. In addition, the tautomeric equilibrium constant was calculated as $K = 9$, thus explaining the initial predominance of the κ*N*(3) linkage isomer in the system. In the absence of dmso, this isomer converts very rapidly into the more stable κ*N*(1) analogue.

TABLE I

Kinetic and equilibrium parameters of the κ*N*(1) and κ*N*(3) linkage isomers of the $[Fe(CN)_5(his)]^{3-}$ complex

	N(1)-his	N(3)-his
Formation reaction		
k_f / dm^3 mol^{-1} s^{-1}	3.2×10^2	3.2×10^2
$\Delta H^{\ddagger}$ / kJ mol^{-1}	6.2×10^1	6.2×10^1
$\Delta S^{\ddagger}$ / J mol^{-1} K^{-1}	2.1×10^1	2.1×10^1
Dissociation reaction		
k_d / s^{-1}	5.3×10^{-4}	1.1×10^{-1}
$\Delta H^{\ddagger}$ / kJ mol^{-1}	1.0×10^2	9.2×10^1
$\Delta S^{\ddagger}$ / J mol^{-1} K^{-1}	4.6×10^1	4.6×10^1
Equilibrium reaction		
K / dm^3 mol^{-1}	5.9×10^{-5}	2.9×10^{-3}
$\Delta H^{\ddagger}$ / kJ mol^{-1}	-4.1×10^1	-2.6×10^1
$\Delta S^{\ddagger}$ / J mol^{-1} K^{-1}	-2.5×10^1	-2.1×10^1

Linkage isomers have also been observed in the reaction of $[Fe(CN)_5(H_2O)]^{3-}$ with methionine and methionine sulfoxide.[202,204] These amino acids, in the anionic form, can bind pentacyanoferrate(II) ions through the available S and NH_2 groups. The kinetics carried out in the presence of the dmso ligand, allowed us to discriminate between the κ*S* and κ*NH*$_2$ linkage isomers, as summarized in Table II.

This study has revealed that although thioether and sulfoxide groups bind preferentially to soft metals, such as the pentacyanoferrate(II) ion, un-

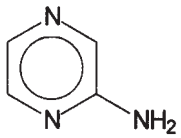
TABLE II

Kinetic and stability constants for the κ*S* and κ*NH*$_2$ linkage isomers of the pentacyanoferrate(II) complex of methionine and methionine sulfoxide

	κ*S* methionine zwitterionic	κ*S* meth$^-$	κ*NH*$_2$ meth$^-$
k_f / dm^3 mol^{-1} s^{-1}	5.4×10^2	1.4×10^2	2.9×10^1
k_d / s^{-1}	4.4×10^{-4}	3.0×10^{-4}	2.1×10^{-2}
K / dm^3 mol^{-1}	1.2×10^6	4.6×10^5	1.3×10^3
	κ*S* SO(methionine) sulfoxide zwitterionic	κ*S* meth$^-$	κ*NH*$_2$ meth$^-$
k_f / dm^3 mol^{-1} s^{-1}	3.1×10^2	7.7×10^1	2.5×10^1
k_d / s^{-1}	1.5×10^{-4}	1.6×10^{-4}	1.9×10^{-2}
K / dm^3 mol^{-1}	2.1×10^6	4.8×10^5	1.3×10^3

der dynamic (non-equilibrium) conditions, the two κ*S* and κ*NH*$_2$ linkage isomers are produced.

Similar studies, using competitive methods, have been carried out for accessing the linkage isomers involving polyaza-heterocyclic ligands, such as 2-aminopyrazine.[205]



2-aminopyrazine (ampz)

The aminopyrazine ligand (ampz) exhibits two potential binding sites represented by the NH_2 group and the opposite N(4) aromatic atom, in addition to a hindered N(1) atom. Stopped flow experiments have demonstrated the initial formation of the two κ*NH*$_2$ and κ*N*(4) linkage isomers.

$$[Fe(CN)_5(H_2O)]^{3-} + \text{ampz} \rightarrow [Fe(CN)_5(\kappa N(4)\{\text{ampz}\})]^{3-} + H_2O \quad (20)$$

$$[Fe(CN)_5(H_2O)]^{3-} + \text{ampz} \rightarrow [Fe(CN)_5(\kappa NH_2\{\text{ampz}\})]^{3-} + H_2O \quad (21)$$

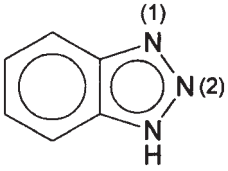
$$[Fe(CN)_5(\kappa NH_2\{\text{ampz}\})]^{3-} \rightleftharpoons [Fe(CN)_5(\kappa N(4)\{\text{ampz}\})]^{3-} \quad (22)$$

The κNH_2 isomer is more labile and less stable than the $\kappa N(4)$ analogue, undergoing slow, complete conversion into the latter. From the competitive kinetics in the presence of dmso, the isomerization constants have been solved as $k_f(\kappa NH_2) = 280\ dm^3\ mol^{-1}\ s^{-1}$, $k_d(\kappa NH_2) = 1.1\ s^{-1}$, $K(\kappa NH_2) = (k_f / k_d) = 2.5\ dm^3\ mol^{-1}$; and $k_f\{\kappa N(4)\} = 280\ dm^3\ mol^{-1}\ s^{-1}$, $k_d\{\kappa N(4)\} = 9.0 \times 10^{-4}\ s^{-1}$, $K\{\kappa N(4)\} = 3.1 \times 10^5\ dm^3\ s^{-1}$.

ELECTROCHEMICAL GENERATION OF LINKAGE ISOMERS

Changes in the oxidation states of metal ions can modify dramatically the relative metal-ligand affinities for the several binding sites involved in the complex. In this way, linkage isomers can be generated in a dynamic way along with cyclic potential scanning, depending on the rates of the substitution or isomerization processes. This is particularly the case of low spin M^{II} (d^6) and M^{III} (d^5) complexes, such as $[Fe(CN)_5L]^{3-/2-}$ and $[Ru(NH_3)_5L]^{2+/3+}$. In the reduced form, the d^6 complexes are strong π-donor species, exhibiting high affinity for π-acceptor ligands such as CO, -S(dmso), and aromatic N-heterocyclic molecules.[199,201,206] This behavior inverts in the oxidized form, in which case the electron-donor capability of the ligand becomes more important.

An interesting case of linkage isomerization has been reported for benzotriazole complexes. Benzotriazole (btH) is an aromatic ligand exhibiting three vicinal N-atoms available for coordination, particularly in the anionic form. It displays remarkable efficiency as a corrosion inhibitor for copper and its alloys.[207] The pK_a of neutral and protonated benzotriazole is 8.6 and 1.6, respectively.[208]



benzotriazole (btH)

The pentacyanoferrate(II) complex forms two linkage isomers with benzotriazole (btH), denoted as $\kappa N(1)$ and $\kappa N(2)$. The two species can be detected by ^1H and ^{13}C NMR spectroscopy, as well as by electrochemical methods.[209] The shapes of the voltamograms are dependent on the potential scan rates (Figure 1).

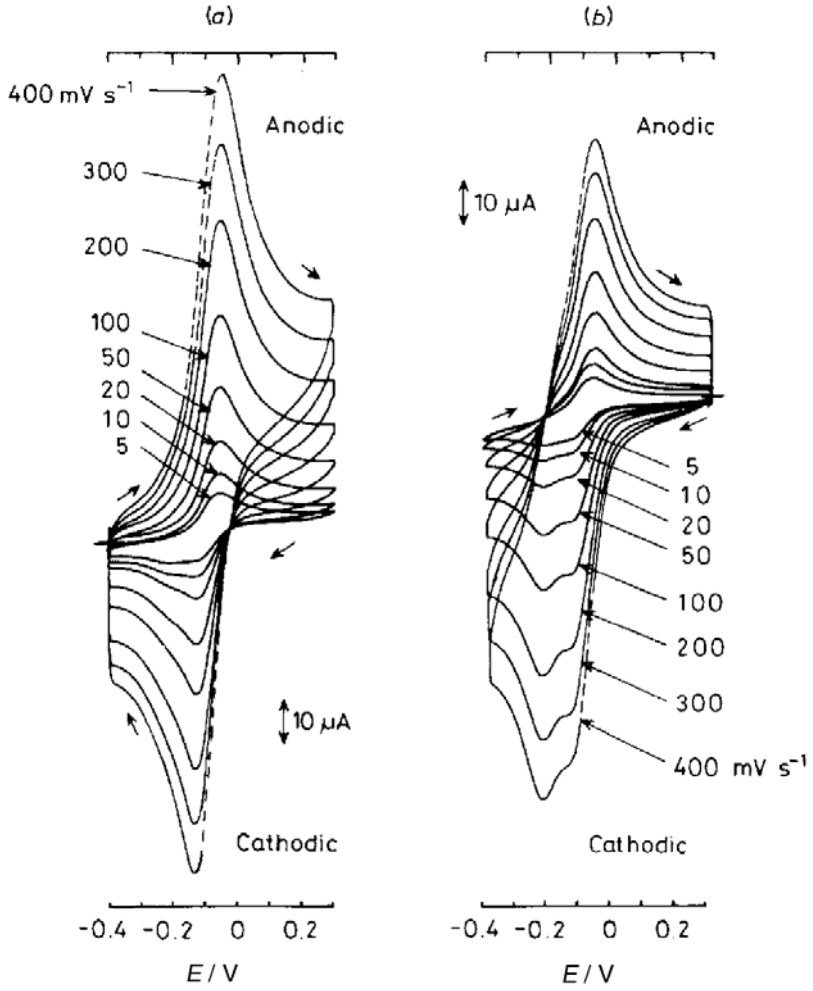


Figure 1. Cyclic voltamograms of $[Ru(NH_3)_5(bt)]^+$ (2.0×10^{-3} mol dm^{-3}, pH = 9, I = 0.5 mol dm^{-3} (KCl), 25 °C) at several potential scan rates, starting from (a) –400 mV and (b) +300 mV after 5 min to ensure complete equilibration in solution. Adapted from Ref. 209.

Starting from the complex in the iron(II) form, at high scan rates (> 200 mV s^{-1}) two waves becomes discernible at $E_{1/2}$ = 0.43 and 0.53 V, corresponding to the κN(1) and κN(2) isomers, respectively. A similar intensity ratio is observed, consistent with an isomerization constant K = 2.40. At intermediate scan rates, *e.g.* 50 mV s^{-1}, the voltamograms can be dealt with as a reversible electrochemical process preceded by a reversible chemical (isomerization) reaction.

$$[Fe^{II}(CN)_5(\kappa N(2)\{btH\})]^{3-} \rightleftharpoons [Fe^{II}(CN)_5(\kappa N(1)\{btH\})]^{3-} \qquad (k_{21},\ k_{12}) \quad (23)$$

$$[Fe^{II}(CN)_5(\kappa N(2)\{btH\})]^{3-} \rightleftharpoons [Fe^{III}(CN)_5(\kappa N(1)\{btH\})]^{2-} + e^- \quad (24)$$

In this case, the kinetic constants of isomerization can be calculated from the Nicholson and Shain equation:[210]

$$(i_d / i) = 1.02 + 0.471(1/K)[a/(k_{12} + k_{21})]^{1/2} \quad (25)$$

where i is the observed current, i_d is the diffusion controlled current, a corresponds to the potential scan rates, $K = k_{12}/k_{21}$. The calculated values at 298 K for k_{12} and k_{21} were 1.55 and 0.65 s^{-1}, respectively.

At slow scan rates (<10 mV s^{-1}) only a single, reversible wave is observed at $E_{1/2}$ = 0.43 V, corresponding to the $\kappa N(1)$ isomer. In this case, as isomer $\kappa N(1)$ is oxidized, the equilibrium is restablished rapidly enough, on the time scale of the cyclic voltammetry, so that a single wave is observed.

Based on the kinetics of formation and substitution reactions in the presence of dmso (in high excess), the rate constants have been calculated as follows:

$$[Fe(CN)_5(H_2O)]^{3-} + btH \rightarrow [Fe(CN)_5(btH)]^{3-} + H_2O \qquad (k_f) \quad (26)$$

$$[Fe(CN)_5(\kappa N(2)\{btH\})]^{3-} \rightleftharpoons [Fe(CN)_5(\kappa N(1)\{btH\})]^{3-} \qquad (K) \quad (27)$$

$$[Fe(CN)_5(\kappa N(2)\{btH\})]^{3-} + dmso \rightarrow [Fe(CN)_5(dmso)]^{3-} + btH \quad (k_{-N(2)}) \quad (28)$$

$$[Fe(CN)_5(\kappa N(1)\{btH\})]^{3-} + dmso \rightarrow [Fe(CN)_5(dmso)]^{3-} + btH \quad (k_{-N(1)}) \quad (29)$$

where k_f = 330 $dm^3\ mol^{-1}\ s^{-1}$; K = 2.40; $k_{-N(2)} = 9.0 \times 10^{-3}\ s^{-1}$; $k_{-N(1)} = 3.7 \times 10^{-3}\ s^{-1}$.

In comparison with the isomerization rates, dissociation of the benzotriazole ligand from the complex is slower by two orders of magnitude. Therefore, the isomerization mechanism in the benzotriazole complex is essentially intramolecular.

In the case of the benzotriazole pentaammineruthenium(II) complex,[211] $[Ru(NH_3)_5(btH)]^{2+}$, the $\kappa N(2)$ predominates in solution, as evident from the NMR and cyclic voltammetry measurements (Figure 1). However, at pH = 9.0, benzotriazole undergoes deprotonation, and cyclic voltammetry behavior becomes rather interesting. By starting from negative potentials, the ruthenium-

benzotriazolate complex is in the reduced form, (Ru^{II}), and only a single anodic peak is observed in the cyclic voltamograms, corresponding to the oxidation of the κ*N*(2) isomer. However, by reversing the potential, two cathodic peaks become discernible, and relative intensities depend upon the scan rates, indicating a dynamic process, very similar to those observed for the benzotriazolepentacyanoferrate(II) case. The two peaks were ascribed to the κ*N*(1) and κ*N*(2) isomers in the ruthenium(III) complex. The equilibrium constants were obtained from the deconvolution of cyclic voltamograms of the oxidized complexes, at high scan rates, as K_{12} = 1.4. The corresponding kinetic constants were extracted using the Nicholson and Shain formalism (Eq. 25), as k_{12} = 0.22 and k_{21} = 0.16 s^{-1}. Starting from the oxidized complexes, by reversing the potential scan, it is possible to monitor, electrochemically, the equilibrium reaction for the reduced species. Based on simple thermodynamic and kinetic considerations, the corresponding equilibrium and kinetic constants have been calculated, as summarized in Table III.

The study has been recently extended to the ruthenium(II/III)-edta complexes of benzotriazole.[212] The starting $[Ru^{III}(edta)(H_2O)]^-$ complex is particularly interesting because of the intrinsic lability of the sixth coordination position.[213] In contrast to the $[Fe(CN)_5(H_2O)]^{3-}$ complex, it reacts with benzotriazole by an associative mechanism. The $[Ru^{III}(edta)(btH)]^-$ complex exhibits pK_a = 5.7. At pH = 4.7, only a single isomeric species was recorded for the ruthenium(III), based on cyclic voltammetry. However, by reversing the potential scan, two isomeric species were detected for the reduced product. The corresponding kinetic and equilibrium constants were extracted as in the case of the pentaammineruthenium complexes (Table III).

As can be seen in Table III, the preferred binding site for the benzotriazole ligand is the N(1) atom, instead of the central N(2) atom. As a matter of fact, according to theoretical calculations for btH,[212] the N(1) atom is more nucleophilic than N(2), thus explaining the predominance of the N(1) isomer in the case of the Fe^{III} and Ru^{III} complexes. On the other hand, the N(2) site becomes competitive in the case of metal ions with a high-back-bonding capability, such as the low-spin iron(II) and ruthenium(II). This is quite evident in the case of the $[Ru^{II}(NH_3)_5(bt)]^+$ complex. Another important conclusion is that isomerization rates are much faster than those for the ligand substitution processes, supporting an intramolecular mechanism where the metal ion migrates from N(1) to N(2) and *vice-versa*, presumably through the formation of fluxional π-bonding interactions.

An intriguing case of long range fluxional behavior has been reported for the linkage isomerization in the κ*N*(amide)-pentaammineruthenium(II) complex with nicotinamide and isonicotinamide ligands.[214] Starting from the κ*N*(amide)-Ru^{III} complex, and reducing rapidly using stopped-flow tech-

TABLE III

Isomerization constants and activation parameters for benzotriazole complexes

Complex	N(i) → N(j)	k_{ij} / s^{-1}	$\Delta H^{\ddagger}$ / kJ mol^{-1}	$\Delta S^{\ddagger}$ / J K^{-1} mol^{-1}	K_{12}	Reference
$[Fe^{II}(CN)_5(btH)]^{3-}$	1 → 2	6.5×10^{-1}	9.9	-2.6×10^{1}	4.2×10^{-1}	209
	2 → 1	1.6	1.2×10^{1}	-1.7×10^{1}		
$[Fe^{III}(CN)_5(btH)]^{2-}$	1 → 2	4.0×10^{-3}	–	–	9.0×10^{-3}	209
	2 → 1	4.4×10^{-1}	–	–		
$[Ru^{II}(edta)(btH)]^{2-}$	1 → 2	1.4×10^{-3}	–	–	3.3×10^{-1}	212
	2 → 1	4.3×10^{-3}	–	–		
$[Ru^{III}(edta)(btH)]^{-}$	–	–	–	–	4.6×10^{-3}	212
$[Ru^{II}(NH_3)_5(bt)]^{+}$	1 → 2	3.9×10^{-2}	–	–	8.3×10^{1}	211
	2 → 1	5.0×10^{-4}	–	–		
$[Ru^{III}(NH_3)_5(bt)]^{2+}$	1 → 2	2.2×10^{-1}	1.5	-5.7×10^{1}	1.4	211
	2 → 1	1.6×10^{-1}	4.7	-4.6×10^{1}		

niques, the corresponding κ*N*(amide)-Ru^{II} complex has been generated in aqueous solution. This species isomerizes to the pyridyl-bonded form at an estimated rate of 9.6 s^{-1}, much higher than the typical substitution rates in pentaammineruthenium(II) complexes, thus supporting an intramolecular mechanism. In contrast to the preceding examples, the Ru^{II} migration is not to a neighboring atom, but rather to a site six bonds away.

In addition to benzotriazole, a few representative examples of vicinal N-containing heterocycles are known. They are basically given by some triazole/triazolate[36,150,215] and tetrazole/tetrazolate derivatives[82,216–222] (the latter have been explored mainly by Purcell and co-workers). On the other hand, metal complexes with typically basic (π-donor) ligands are much more abundant in the literature. The reported cases include imidazole/imidazolate and imidazole-like species, and their biological relatives as well.[44,56,58,69,203,223–250]

DIMETHYL SULFOXIDE AND RELATED LIGANDS

Because of the contrasting binding properties of the S and O atoms, dimethyl sulfoxide (dmso) can form κ*S* and κ*O* linkage isomers, depending on the nature and characteristics of the transition metal ions. The sulfinyl group provides a good acceptor site for π-electron donor species, such as low spin iron(II) and ruthenium(II) ions, while the oxygen atom is the preferred site for hard metals, such as the 3d trivalent cations, Al^{3+} and lanthanides. While most of the Ru^{II} complexes exhibit a great affinity for sulfur ligands, the preference demonstrated by the corresponding Ru^{III} species is usually inverted, favoring the binding of the O-donor sites. Classical examples are based on the $[Ru(NH_3)_5(\text{sulfoxide-ligand})]^{2+/3+}$ systems.[67,71,72,251]

Indeed, the $[Ru(NH_3)_5(dmso)]^{2+}$ complex is a good example of electrochemically driven linkage isomerization involving sulfoxide ligands. In the reduced form, the dmso ligand is coordinated by the S atom, *i.e.* $[Ru(NH_3)_5(\kappa S\{dmso\})]^{2+}$, as a consequence of the remarkable π-backbonding properties of the ruthenium(II) ion. High stabilization of the reduced complex is reflected in its high E^o value, *i.e.* 1.0 V. Oxidation of the complex with Ce^{IV} ions leads to κ*S* to κ*O* linkage isomerization, giving rise to a new wave at 0.01 V in cyclic voltamograms. The κ*S*→κ*O* isomerization rates for the $[Ru(NH_3)_5(dmso)]^{3+}$ complex were obtained by the method of Nicholson and Shain as $k_{S\rightarrow O} = 0.070\ s^{-1}$. For the related methionine sulfoxide complex, the electrochemical behavior was very similar, and the isomerization constant was found to be $k_{S\rightarrow O} = 0.24\ s^{-1}$. The κ*O*→κ*S* isomerization in the Ru^{II} complex is accompanied by a parallel aquation reaction, but the rates were estimated at 30 and 70 s^{-1} for the dmso and methionine sulfoxide complexes respectively.[72]

A related case is represented by the $[Ru^{III}(edta)(dmso)]^-$ complex.[252] In contrast to the pentaammine analogue, dmso coordinates to the $[Ru^{III}(edta)]^-$ moiety through the S atom; however, the formation constant of $[Ru^{III}(edta)(\kappa S\{dmso\})]^-$ is rather small (K = 1.8 dm^3 mol^{-1}), thus requiring a very large excess of dmso over the starting $[Ru^{III}(edta)H_2O]^-$ complex. The reduced complex is extraordinarily stable ($K = 7.7 \times 10^9$ dm^3 mol^{-1}), corresponding to the κS isomer. In the presence of a concentration of dmso above 3 mol dm^{-3}, the cyclic voltamograms are typically reversible, exhibiting a single pair of waves at $E_{1/2}$ = 0.56 V. Below 1 mol dm^{-3} dmso, the $[Ru^{III}(edta)(\kappa S\{dmso\})]^-$ complex undergoes aquation, giving rise to a new reversible wave at $E_{1/2}$ = –0.010 V, corresponding to the $[Ru^{III}(edta)H_2O]^-$ complex.

An interesting example of electrochemically driven linkage isomerization in dimethyl sulfoxide complexes is given by the *all cis*-$[RuCl_2(\kappa S\{dmso\})_2(tbpy)_2]$ complex, where tbpy = *tert*-butylpyridine.[253] Starting from the reduced complex in acetonitrile solutions, and scanning in the direction of positive potentials, its corresponding cyclic voltamograms (Figure 2) show a single reversible peak observed at $E_{1/2}$ = 1.27 V *versus* SHE, ascribed to the $Ru^{III/II}$ couple.

In the reverse scan, the corresponding cathodic peak current becomes less intense, and a new peak grows at $E_{1/2}$ = 0.55 V. Starting from the oxidized complex, two reversible waves are observed at 1.27 and 0.55 V. The dramatic change of $E_{1/2}$ is consistent with the conversion of the κS isomer to the κO analogue, in the Ru^{III} complexes, according to the reversible equilibrium:

$$Ru^{III}(\kappa O\{dmso\}) \rightleftharpoons Ru^{III}(\kappa S\{dmso\}) \qquad (K^{III}) \qquad (30)$$

$$\updownarrow 0.55\ V \qquad \updownarrow 1.27\ V$$

$$Ru^{II}(\kappa O\{dmso\}) \rightleftharpoons Ru^{II}(\kappa S\{dmso\}) \qquad (K^{II}) \qquad (31)$$

The equilibrium constants were calculated from the relative ratios of the cathodic peak currents recorded at high scan rates, *i.e.* $K^{III}_{O\rightarrow S}$ = 0.63. Based on the equation proposed by Nicholson and Shain for a reversible chemical reaction preceding an electrochemical step, the isomerization constants were calculated as $k^{III}_{O\rightarrow S}$ = 1.2 s^{-1} and $k^{III}_{S\rightarrow O}$ = 1.9 s^{-1}. These rates are at least five orders of magnitude higher than the typical substitution rates in this type of complex, supporting an intramolecular isomerization mechanism like in the case of the benzotriazole complexes.

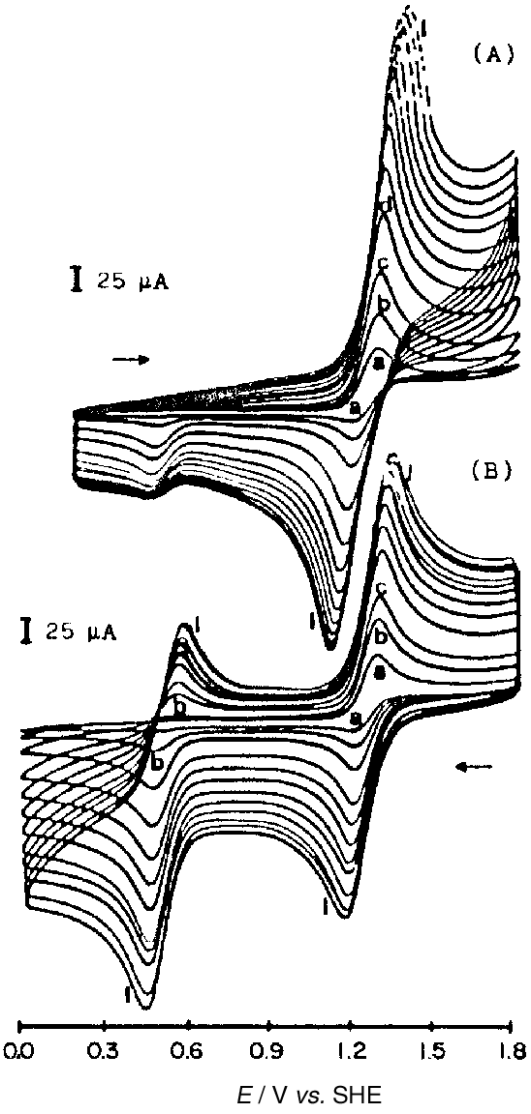


Figure 2. Cyclic voltamograms of *ccc*-[$RuCl_2(dmso)_2(tbpy)_2$] (1 mmol dm^{-3}), starting at (A) 0.2 V and (B) 1.8 V, at (a) 20, (b) 50, (c) 100, (d) 200, (e) 300, (f) 400, (g) 500, (h) 600, (i) 700, (j) 800, (k) 900, and (l) 1000 mV s^{-1} (acetonitrile, 25 °C, [TEAP] = 0.10 mol dm^{-3}). Adapted from Ref. 253.

By solving the square scheme, the equilibrium constant for the Ru^{II} complex was 2.1×10^{12}, favoring the formation of the κ*S* isomer. Evaluation of the kinetic constants for the isomerization reaction in the Ru^{II} complex can

be carried out by monitoring the decay of the unstable $Ru^{II}(\kappa O\{dmso\})$ species, along with the conversion process into the $Ru^{II}(\kappa S\{dmso\})$ form. A simple way of generating the $Ru^{II}(\kappa O\{dmso\})$ isomer is to start from the mixture of $Ru^{III}(\kappa O\{dmso\})$ and $Ru^{III}(\kappa S\{dmso\})$ isomers in equilibrium, *e.g.* at 1.8 V. By applying a fast potential scanning in the cathodic direction, the $Ru^{II}(\kappa O\{dmso\})$ species is generated, and can be monitored as a function of time (or scan rates). Its decay proceeds according to an exponential equation, consistent with the isomerization rate constant $k^{II}_{O\rightarrow S} = 0.010\ s^{-1}$. Based on the calculated equilibrium constant, from the square scheme, the reverse isomerization constant was obtained as $k^{II}_{S\rightarrow O} = 5 \times 10^{-14}\ s^{-1}$.

It is interesting to note that the related *cis,cis,trans*-$[RuCl_2(\kappa S\{dmso\})_2(tbpy)_2]$ complex,[253] exhibiting two *trans*-Cl-Ru^{III}-$(\kappa S\{dmso\})$ bonds, is not susceptible to electrochemically driven linkage isomerization processes, presumably because of the high stability provided by the *trans* cooperative interactions involving the π-donor Cl^- ligand and the π-acceptor $(\kappa S\{dmso\})$ ligand. In contrast, the *all cis* isomer isomerizes very rapidly to the O-bound form when it is oxidized to Ru^{III}. The main difference between these two isomers is the occurrence, in the latter, of a *trans*-$(\kappa S\{dmso\})$-Ru-tbpy bond, in addition to a stable *trans*-Cl-Ru^{III}-$(\kappa S\{dmso\})$ bond. The presence of two π-acceptor ligands in *trans*-position seems to weaken the Ru^{III}-$(\kappa S\{dmso\})$ bond, promoting its rapid isomerization into the Ru^{III}-$(\kappa O\{dmso\})$ form.

Electrochemically driven linkage isomerization reactions have also been reported for the triangular μ-oxo-ruthenium-acetate cluster, $[Ru_3O(Ac)_6(py)_2(dmso)]^+$.[254] The species exhibits a trinuclear structure containing ruthenium ions in the formal (3+) oxidation state, kept together by a strong interaction with a central oxygen atom and six bridging acetate ligands. In fact, the electronic structure is strongly delocalized by means of metal-metal bonds. According to the vibrational and NMR spectra, the dmso ligand is coordinated to the ruthenium center by means of the O atom.

Cyclic voltamograms have been measured in acetonitrile solutions, in the presence of a high excess of the dmso ligand, in order to prevent its dissociation from the complex. In this case, starting from the $Ru^{III}Ru^{III}Ru^{II}(\kappa O\{dmso\})$ complex at 0.8 V, and scanning the potential in the direction of negative potentials, a single cathodic peak was observed at $E_{1/2} = 0.13$ V, corresponding to the formation of the $Ru^{III}Ru^{III}Ru^{II}(\kappa O\{dmso\})$ species. In the reverse scan, in addition to the corresponding oxidation peak, another peak becomes evident at $E_{1/2} = 0.42$ V, associated with the formation of the $Ru^{III}Ru^{III}Ru^{II}(\kappa S\{dmso\})$ isomer. Starting from the reduced complex at –0.5 V, the relative intensities of the pair of waves at 0.13 and 0.42 V are inverted, indicating that the $Ru^{III}Ru^{III}Ru^{II}(\kappa S\{dmso\})$ isomer predominates

over the $Ru^{III}Ru^{III}Ru^{II}(\kappa O\{dmso\})$ one. This system can be treated in terms of the square scheme and of the Nicholson and Shain procedure, in order to extract the equilibrium and kinetic isomerization constants, as shown below:

$$\begin{array}{ccc} Ru^{III}Ru^{III}Ru^{III}(\kappa O\{dmso\}) & \rightleftharpoons & Ru^{III}Ru^{III}Ru^{III}(\kappa S\{dmso\}) \quad (k^{III}_{S\to O}, k^{III}_{O\to S}) \\ \downarrow\uparrow 0.13\ V & & \downarrow\uparrow 0.42\ V \\ Ru^{III}Ru^{III}Ru^{II}(\kappa O\{dmso\}) & \rightleftharpoons & Ru^{III}Ru^{III}Ru^{II}(\kappa S\{dmso\}) \quad (k^{II}_{S\to O}, k^{II}_{O\to S}) \end{array} \qquad (32)$$

(33)

where $k^{III}_{S\to O} = 1.2 \times 10^{-5}\ s^{-1}$, $k^{III}_{O\to S} = 1.5 \times 10^{-1}\ s^{-1}$, and $K^{III}_{O\to S} = 8.1 \times 10^{-5}$; $k^{II}_{S\to O} = 1.5\ s^{-1}$, $k^{II}_{O\to S} = 2.3 \times 10^{-1}\ s^{-1}$, and $K^{II}_{O\to S} = 6.5$.

The isomerization rates for the oxidized and reduced clusters are much faster than the usual rates of substitution reactions, evidencing an intramolecular mechanism.

Although there are some other dmso-metal complexes for which linkage isomerism has been reported,[21,35,68,71,72,255–257] only a reduced number of them were studied according to a similar electrochemical approach as described above, or they display comparable redox behavior as well.

Another rather interesting case of linkage isomerization involves the formation of π-complexes of $[Os(NH_3)_5]^{2+}$ directly coordinated with the C=C bond in functionalized aromatic rings, after reduction of the corresponding osmium(III) complexes coordinated at the functional groups. The isomerization process is directed by the special affinity of the π-donating species $[Os(NH_3)_5]^{2+}$ to unsaturated groups, such as C=C, and proceeds *via* an intramolecular mechanism.[258–260]

pH-INDUCED FORMATION OF LINKAGE ISOMERS

Both κ*O* and κ*N* amide complexes have been reported in the literature.[26,68,73,74,76,78,79,81,84,85,226,229,230,241–244,248,261–298] Although there are many published materials on this class of systems, herein we will focus our attention on a couple of illustrative systems, based on ammineruthenium complexes. Linkage isomerization in the pentaammineruthenium(III) complexes[280] takes place in accordance with the following scheme:

$$[(NH_3)_5Ru^{III}(\kappa O\{OC(NH_2)R\})]^{3+} \rightleftharpoons [(NH_3)_5Ru^{III}(\kappa N\{OC(NH_2)R\})]^{3+} \quad (K_{O\rightarrow N})$$
$$\downarrow\uparrow \; pKa > 10 \qquad\qquad \downarrow\uparrow \; pKa < 2.5 \qquad (34)$$

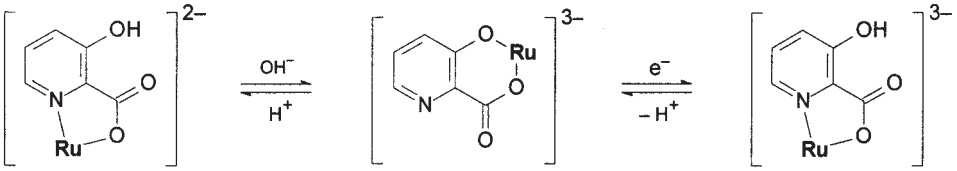
$$[(NH_3)_5Ru^{III}(\kappa O\{OC(NH)R\})]^{2+} \rightleftharpoons [(NH_3)_5Ru^{III}(\kappa N\{OC(NH)R\})]^{2+} \quad (K_{O\rightarrow N})$$
$$+ H^+ \qquad\qquad + H^+ \qquad (35)$$

The κ*O* isomer is thermodynamically more stable than the κ*N* one, however it usually undergoes substitution by coordinating solvents, such as H_2O, dmf and dmso, in acidic media, and rearranges to the deprotonated N-bonded form in basic or neutral solutions. In fact, the N-bonded form is very acidic ($pK_a < 2.5$), while the O-bonded form has an estimated $pK_a > 10$. Cyclic voltammetry in basic solution is consistent with reversible $Ru^{III/II}$ couples for the substitution-inert deprotonated form $[(NH_3)_5Ru(\kappa N\{OC(NH)R\})]^{2+/+}$; however, the reduced Ru^{II} species undergoes protonation in acid and neutral solutions ($pK_a \approx 7$) and isomerizes to the O-bonded amide. Following oxidation to Ru^{III}, isomerization of the O-bonded amides back to the N-bonded amides is driven by the selective deprotonation to $[(NH_3)_5Ru^{III}(\kappa N\{OC(NH)R\})]^{2+}$, as shown in the scheme above. The substitution lability of O-bonded amides in coordinating solvents, tautomerization of N-bonded amides on Ru^{III}, and catalysis by Ru^{II} and the base complicate measurements of the rates for linkage isomerizations.

Analogously, when *cis*-$[Ru(NH_4)_4(H_2O)_2]^{3+}$, in slightly alkaline solution, reacts with any of the three amides, glycylglycine, glycinamide and *N′*-ethylglycinamide, a chelate tetraammineruthenium(III) complex is obtained, involving the N,N′ atoms of the amino and amide groups.[299,300] The uncatalyzed transformation of these chelates to the κ*N,O* forms is slow, but it is feasible by reducing the complex to the (2+) state in acidic solution, and reoxidizing. Such chelates are labile in the Ru^{II} form. Therefore, the presence of Ru^{II} promotes labilization of the Ru^{III} species *via* electron transfer, allowing determination of the equilibrium quotients for the κ*N,N′* and κ*N,O* forms. For glycinamide as the ligand, the isomerization equilibrium constant for the Ru^{II} complex is $K_{N,N'\rightarrow NO} = 1.6 \times 10^{-4}$, when both isomers are protonated. However, as the pH is raised, the κ*N,N′* chelate becomes more stable, because it involves a relatively more acidic site. In the case of the Ru^{III} complex, the equilibrium ratio $[Ru^{III}(\kappa N,O)]/[Ru^{III}(\kappa N,N')][H^+]$ is 16. As the pH is raised, the κ*N,N′* chelate becomes more stable.

Another interesting case of pH induced chelate linkage isomerization has been observed[301] for the ruthenium(III)-edta complex with the 3-hydroxy-

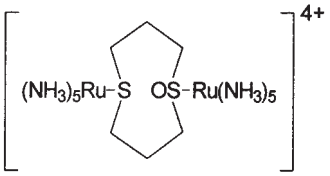
picolinate ligand ($Hhpic^-$). At pH = 5, the complex is practically colorless and can be represented by the $[Ru^{III}(edta)(\kappa N,O\{Hhpic\})]^{2-}$ complex. At pH > 9, deprotonation of the phenolic group promotes an intramolecular linkage isomerization, generating the faint red $[Ru^{III}(edta)(\kappa O,O\{hpic\})]^{3-}$ complex. Isomerization kinetics was monitored based on the pH jump experiments, exhibing typically first order behavior, with $k_{N,O\rightarrow O,O} = 4.7 \times 10^{-3}$ s^{-1}. The lack of dependence on the $hpic^{2-}$ concentration supports an intramolecular isomerization mechanism, where, after the rupture of the Ru-N(pyridine) bond, the attached ruthenium(III) complex undergoes a rapid rotation through the carboxylate group, in order to bind to the phenolate site. It should be noted that both isomers can be electrochemically reduced, but converting into a single deep red $[Ru^{II}(edta)(\kappa N,O\{Hhpic\})]^{3-}$ complex, strongly stabilized by the ruthenium-to-pyridinecarboxylate charge-transfer interactions.



Many other linkage isomerization studies are also found in literature. Excluding the nitro-nitrito and thiocyanate related systems, most of them concern amide derivatives[26,68,73,74,76,78,79,81,84,85,226,229,230,241–244,248,261–298] which have been investigated mainly by Jackson, Sargeson and co-workers) and/or a large collection of coordination complexes containing polyfunctional ligands,[53,73,75,292,302–315] which also include oximes/imines,[73,74306–308,316–328] and sulfinate species.[19,20,26,29,30,32,329–336] A significant number of investigations on nitrosyl-metals[23,24,47,49,59,60,62,152,217,337–343] have also emerged recently.

FINAL REMARKS

Linkage isomerization has been one of the most intriguing aspects in coordination chemistry, since the classical, fundamental discovery by Alfred Werner. Only recently, however, changes in the optical, electrochemical and kinetic properties associated with the linkage isomerization process have been exploited for the design of molecular switches and memory devices[344] as well for the nanotechnology applications.[345–350] A remarkable example is the electrochemical hysteresis reported by Sano and Taube[67,251] for the asymmetric binuclear (1,5-dithiocyclooctane 1-oxide) bis(pentaammineruthenium) complex.



In this system, a reversible $Ru^{II/III}$ couple bound to a thioether group is combined with another $Ru^{II/III}$ couple bound to a sulfoxide function, which is susceptible to linkage isomerization on electron transfer. When the molecule is fully reduced, the following representation applies: Ru^{II}–S~~(O)S–Ru^{II}. By increasing the potential, the Ru^{II}–S site gets oxidized first (E° = 0.58 V), generating the stable mixed valence complex Ru^{III}–S~~(O)S–Ru^{II}. At E = 1.04 V, a second oxidation takes place at the Ru^{II}–SO site, yielding the thermodynamically meta-stable species, Ru^{III}–S~~(O)S–Ru^{III}, which undergoes linkage isomerization, converting into the Ru^{III}–S~~SO–Ru^{III} product ($k^{III}_{S\rightarrow O}$ = 13 s^{-1}). In the reverse scan, since the last process takes place within the time scale of cyclic voltammetry, the cathodic component of the redox wave at 1.04 V practically disappears. At E° = 0.65 V, the Ru^{III}–S~~SO–Ru^{III} species undergoes a reversible reduction at the Ru^{III}–S site, yielding Ru^{II}–S~~SO–Ru^{III}. The final reduction process takes place at E° = 0.03 V, involving the O-bound ruthenium moiety, generating a rather unstable Ru^{II}–S~~SO–Ru^{II} species. Now, the Ru^{II}–OS moiety undergoes a linkage isomerization to the S-bound form ($k^{II}_{O\rightarrow S}$ = 3.8 s^{-1}), regenerating the starting complex. It has also been proposed that the mixed-valence state, Ru^{III}–S~~SO–Ru^{II}, can also convert to the Ru^{II}–S~~(O)S–Ru^{II} form, but to a minor extent, by intramolecular electron transfer. The electrochemical hysteresis arises from the fact that the cyclic oxidation and reduction steps do not follow the same route, so that the current response suffers a delay associated with the linkage isomerization process.

REFERENCES

1. G. L. Leigh (Ed.), *Nomenclature of Inorganic Chemistry – Recommendations*, International Union of Pure and Applied Chemistry, Blackwell Science Pub., London, 1990, p. 98.
2. A. Werner, *Ber.* **40** (1907) 765.
3. R. T. M. Fraser, *Linkage Isomerism*, in: G. B. Kauffman (Ed.), *Werner Centennial*, Advances in Chemistry Series, Vol. 62, American Chemical Society, Washington, DC, 1967, p. 295.
4. R. V. Penland, T. J. Lane, and J. V. Quagliano, *J. Am. Chem. Soc.* **80** (1958) 527.
5. K. Nakamoto, J. Fujita, and H. Murata, *J. Am. Chem. Soc.* **80** (1958) 4817.
6. W. H. Hohman, *J. Chem. Educ.* **51** (1974) 553.

7. W. G. Jackson, G. A. Lawrance, P. A. Lay, and A. M. Sargeson, *J. Chem. Educ.* **58** (1981) 734.
8. W. G. Jackson, *J. Chem. Educ.* **68** (1991) 903.
9. W. M. Phillips, S. H. Choi, and J. A. Larrabee, *J. Chem. Educ.* **67** (1990) 267.
10. R. J. Balahura and N. A. Lewis, *Coord. Chem. Rev.* **20** (1976) 109.
11. D. A. Buckingham, *Coord. Chem. Rev.* **135** (1994) 587.
12. J. L. Burmeister, *Coord. Chem. Rev.* **3** (1968) 225.
13. R. A. Bailey, S. L. Kozak, T. W. Michelsen, and W. N. Mills, *Coord. Chem. Rev.* **6** (1971) 407.
14. G. B. Kauffman, *Coord. Chem. Rev.* **11** (1973) 161.
15. J. L. Burmeister, *Coord. Chem. Rev.* **1** (1966) 205.
16. M. A. Hitchman and G. L. Rowbottom, *Coord. Chem. Rev.* **42** (1982) 55.
17. F. Basolo and R. G. Pearson, *Mechanisms of Inorganic Reactions*, John Wiley, New York, 1967, p. 293.
18. W. G. Jackson and A. M. Sargeson, *Rearrangements in Coordination Complexes*, in: P. de Mayo (Ed.), *Rearrangements in Ground and Excited States*, Vol. 2, Academic Press, New York, 1980, p. 273.
19. F. M. D. Akhter, M. Kojima, M. Hirotsu, S. Kashino, and Y. Yoshikawa, *Chem. Lett.* (1994) 2393.
20. F. M. Akhter, M. Hirotsu, I. Sugimoto, M. Kojima, S. Kashino, and Y. Yoshikawa, *Bull. Chem. Soc. Jpn.* **69** (1996) 643.
21. E. Alessio, P. Faleschini, A. S. O. Santi, G. Mestroni, and M. Calligaris, *Inorg. Chem.* **32** (1993) 5756.
22. E. V. Boldyreva, A. V. Virovets, L. P. Burleva, V. E. Dulepov, and N. V. Podberezskaya, *J. Struct. Chem.* **34** (1993) 602.
23. D. V. Fomitchev and P. Coppens, *Comments. Inorg. Chem.* **21** (1999) 131.
24. D. V. Fomitchev, P. Coppens, T. S. Li, K. A. Bagley, L. Chen, and G. B. Richter-Addo, *Chem. Commun.* (1999) 2013.
25. S. C. Gibney, G. Ferraudi, and M. Shang, *Inorg. Chem.* **38** (1999) 2898.
26. W. G. Jackson, S. S. Jurisson, and M. A. Oleary, *Inorg. Chem.* **32** (1993) 445.
27. D. A. Johnson and K. A. Pashman, *Inorg. Nucl. Chem. Lett.* **11** (1975) 23.
28. D. A. Johnson and V. C. Dew, *Inorg. Chem.* **18** (1979) 3273.
29. M. Kojima, Y. Shimizu, K. Nakajima, K. Nakajima, and Y. Yoshikawa, *Bull. Chem. Soc. Jpn.* **67** (1994) 869.
30. M. Kojima and Y. Yoshikawa, *J. Chromatogr. A* **789** (1997) 273.
31. M. Kubota and S. Ohba, *Acta Crystallogr., Sect. B* **48** (1992) 627.
32. M. Murata, M. Kojima, A. Hioki, M. Miyagawa, M. Hirotsu, K. Nakajima, M. Kita, S. Kashino, and Y. Yoshikawa, *Coord. Chem. Rev.* **174** (1998) 109.
33. B. J. Palmer and R. H. Hill, *J. Photochem. Photobiol. A* **72** (1993) 243.
34. H. Seki, K. Okada, Y. Iimura, and M. Hoshino, *J. Phys. Chem. A* **101** (1997) 8174.
35. M. K. Smith, J. A. Gibson, C. G. Young, J. A. Broomhead, P. C. Junk, and F. R. Keene, *Eur. J. Inorg. Chem.* (2000) 1365.
36. R. Wang, J. G. Vos, R. H. Schmehl, and R. Hage, *J. Am. Chem. Soc.* **114** (1992) 1964.
37. K. Yamanari, Y. Kushi, A. Fuyuhiro, and S. Kaizaki, *J. Chem. Soc., Dalton Trans.* (1993) 403.
38. K. Yamanari, M. Kida, M. Yamamoto, T. Fujihara, A. Fuyuhiro, and S. Kaizaki, *J. Chem. Soc., Dalton Trans.* (1996) 305.
39. M. A. Bennett, M. Bown, and M. J. Byrnes, *J. Organomet. Chem.* **571** (1998) 139.

40. E. Boldyreva, J. Kivikoski, and J. A. K. Howard, *Acta Crystallogr., Sect. B* **53** (1997) 394.
41. D. A. Buckingham, C. R. Clark, G. F. Liddell, and J. Simpson, *Aust. J. Chem.* **46** (1993) 503.
42. R. J. Cosmano and J. E. House, *Thermochim. Acta* **13** (1975) 127.
43. M. J. Coyer, R. H. Herber, J. Chen, M. Croft, and S. P. Szu, *Inorg. Chem.* **33** (1994) 716.
44. R. Dalbies, M. Boudvillain, and M. Leng, *Nucleic Acids Res.* **23** (1995) 949.
45. D. J. Darensbourg, J. C. Yoder, M. W. Holtcamp, K. K. Klausmeyer, and J. H. Reibenspies, *Inorg. Chem.* **35** (1996) 4764.
46. A. Delmedico, P. R. Auburn, E. S. Dodsworth, A. B. P. Lever, and W. J. Pietro, *Inorg. Chem.* **33** (1994) 1583.
47. J. L. Hubbard, C. R. Zoch, and W. L. Elcesser, *Inorg. Chem.* **32** (1993) 3333.
48. N. E. Kob and J. E. House, *Transition Met. Chem.* **19** (1994) 31.
49. D. Ooyama, N. Nagao, H. Nagao, Y. Miura, A. Hasegawa, K. Ando, F. S. Howell, M. Mukaida, and K. Tanaka, *Inorg. Chem.* **34** (1995) 6024.
50. A. M. Allgeier and C. A. Mirkin, *Angew. Chem., Int. Ed. Engl.* **37** (1998) 894.
51. A. M. Bond, R. Colton, D. A. Fiedler, L. D. Field, T. A. He, P. A. Humphrey, C. M. Lindall, F. Marken, A. F. Masters, H. Schumann, K. Suhring, and V. Tedesco, *Organometallics* **16** (1997) 2787.
52. C. J. Da Cunha, E. S. Dodsworth, M. A. Monteiro, and A. B. P. Lever, *Inorg. Chem.* **38** (1999) 5399.
53. A. Delmedico, W. J. Pietro, and A. B. P. Lever, *Inorg. Chim. Acta* **281** (1998) 126.
54. W. D. Harman and H. Taube, *J. Am. Chem. Soc.* **110** (1988) 5403.
55. W. D. Harman, M. Sekine, and H. Taube, *J. Am. Chem. Soc.* **110** (1988) 2439.
56. A. Johnson, L. A. Oconnell, and M. J. Clarke, *Inorg. Chim. Acta* **210** (1993) 151.
57. R. A. Leising, S. A. Kubow, L. F. Szczepura, and K. J. Takeuchi, *Inorg. Chim. Acta* **245** (1996) 167.
58. W. H. Myers, J. I. Koontz, and W. D. Harman, *J. Am. Chem. Soc.* **114** (1992) 5684.
59. D. Ooyama, H. Nagao, N. Nagao, F. S. Howell, and M. Mukaida, *Chem. Lett.* (1996) 759.
60. D. Ooyama, H. Nagao, K. Ito, N. Nagao, F. S. Howell, and M. Mukaida, *Bull. Chem. Soc. Jpn.* **70** (1997) 2141.
61. P. Riccieri, E. Zinato, M. Rievaj, D. Bustin, and S. Mesaros, *Inorg. Chim. Acta* **255** (1997) 229.
62. M. Rievaj, E. Korgova, and D. Bustin, *Collect. Czech. Chem. Commun.* **58** (1993) 1371.
63. M. Rievaj, E. Korgova, and D. Bustin, *Collect. Czech. Chem. Commun.* **58** (1993) 530.
64. M. Rievaj, E. Korgova, and D. Bustin, *Collect. Czech. Chem. Commun.* **58** (1993) 328.
65. M. Rievaj, D. Bustin, J. Mocak, P. Riccieri, and E. Zinato, *Inorg. Chim. Acta* **216** (1994) 113.
66. M. Rievaj, D. Bustin, P. Riccieri, and E. Zinato, *Inorg. Chim. Acta* **228** (1995) 153.
67. M. Sano and H. Taube, *J. Am. Chem. Soc.* **113** (1991) 2327.
68. M. Sano, H. Sago, and A. Tomita, *Bull. Chem. Soc. Jpn.* **69** (1996) 977.
69. I. Sovago, A. Kiss, and B. Lippert, *J. Chem. Soc., Dalton Trans.* (1995) 489.
70. A. P. Szecsy and A. Haim, *J. Am. Chem. Soc.* **104** (1982) 3063.
71. A. Tomita and M. Sano, *Inorg. Chem.* **33** (1994) 5825.

72. A. Yeh, N. Scott, and H. Taube, *Inorg. Chem.* **21** (1982) 2542.
73. P. M. Angus and W. G. Jackson, *Inorg. Chem.* **33** (1994) 477.
74. P. M. Angus and W. G. Jackson, *Inorg. Chem.* **35** (1996) 7196.
75. A. Delmedico, S. S. Fielder, A. B. P. Lever, and W. J. Pietro, *Inorg. Chem.* **34** (1995) 1507.
76. D. P. Fairlie, P. M. Angus, M. D. Fenn, and W. G. Jackson, *Inorg. Chem.* **30** (1991) 1564.
77. L. H. Piao, F. Kai, M. Hirohata, I. Moritake, Y. Nakano, and S. Era, *Polyhedron* **16** (1997) 3033.
78. C. Adamo and F. Lelj, *Chem. Phys. Lett.* **223** (1994) 54.
79. P. M. Angus and W. G. Jackson, *Inorg. Chim. Acta* **268** (1998) 85.
80. J. L. Burmeister, R. L. Hassel, and R. J. Phelan, *Inorg. Chem.* **10** (1971) 2032.
81. R. Cini, F. P. Fanizzi, F. P. Intini, G. Natile, and C. Pacifico, *Inorg. Chim. Acta* **251** (1996) 111.
82. S. Hubinger and W. L. Purcell, *Inorg. Chem.* **30** (1991) 3707.
83. W. G. Jackson, G. A. Lawrance, P. A. Lay, and A. M. Sargeson, *Aust. J. Chem.* **35** (1982) 1561.
84. Y. A. Lee, Y. K. Chung, and Y. S. Sohn, *Inorg. Chem.* **38** (1999) 531.
85. F. Lelj and C. Adamo, *Theor. Chim. Acta* **91** (1995) 199.
86. M. Mares, D. A. Palmer, and H. Kelm, *Inorg. Chim. A-Article* **60** (1982) 123.
87. M. Onyszchuk and I. Wharf, *J. Organomet. Chem.* **249** (1983) C9.
88. R. K. Murmann and H. Taube, *J. Am. Chem. Soc.* **78** (1956) 4886.
89. F. Basolo and G. S. Hammaker, *J. Am. Chem. Soc.* **82** (1960) 1001.
90. F. Basolo and G. S. Hammaker, *Inorg. Chem.* **1** (1962) 1.
91. J. R. Ferraro and L. Fabbrizzi, *Inorg. Chim. Acta* **26** (1978) L15.
92. M. Mares, D. A. Palmer, and H. Kelm, *Inorg. Chim. Acta* **27** (1978) 153.
93. I. Grenthe and E. Nordin, *Inorg. Chem.* **18** (1979) 1869.
94. I. Grenthe and E. Nordin, *Inorg. Chem.* **18** (1979) 1109.
95. W. G. Jackson, G. A. Lawrance, P. A. Lay, and A. M. Sargeson, *Inorg. Chem.* **19** (1980) 904.
96. H. D. Abruna, J. L. Walsh, T. J. Meyer, and R. W. Murray, *Inorg. Chem.* **20** (1981) 1481.
97. W. G. Jackson, G. A. Lawrence, P. A. Lay, and A. M. Sargeson, *J. Chem. Soc., Chem. Commun.* (1982) 70.
98. W. Rindermann, R. Vaneldik, and H. Kelm, *Inorg. Chim. Acta Articles* **61** (1982) 173.
99. S. Balt, H. Kuipers, and W. E. Renkema, *J. Chem. Soc., Dalton Trans.* (1983) 1739.
100. K. Miyoshi, N. Katoda, and H. Yoneda, *Inorg. Chem.* **22** (1983) 1839.
101. E. V. Boldyreva, A. A. Sidelnikov, and N. Z. Lyakhov, *Thermochim. Acta* **92** (1985) 109.
102. I. N. Timonova, E. A. Kravtsova, E. V. Boldyreva, and L. N. Mazalov, *J. Struct. Chem.* **28** (1987) 518.
103. M. E. Bartram and B. E. Koel, *J. Vac. Sci. Technol., A* **6** (1988) 782.
104. A. M. Heyns and D. Dewaal, *Spectrochim. Acta, Part A* **45** (1989) 905.
105. C. M. Gordon, R. D. Feltham, and J. J. Turner, *J. Phys. Chem.* **95** (1991) 2889.
106. N. V. Podberezskaya, A. V. Virovets, and E. V. Boldyreva, *J. Struct. Chem.* **32** (1991) 693.
107. A. Massaferro, M. Queirolo, and B. Sienra, *An. Quim.* **88** (1992) 230.

108. J. L. Hubbard, C. R. Zoch, and W. L. Elcesser, *Inorg. Chem.* **32** (1993) 4670.
109. E. Boldyreva, H. Ahsbahs, and H. Uchtmann, *Ber. Bunsenges. Phys. Chem.* **98** (1994) 738.
110. V. E. Dulepov and E. V. Boldyreva, *React. Kinet. Catal. Lett.* **53** (1994) 289.
111. N. Masciocchi, A. Kolyshev, V. Dulepov, E. Boldyreva, and A. Sironi, *Inorg. Chem.* **33** (1994) 2579.
112. A. V. Virovets, E. V. Boldyreva, L. P. Burleva, V. E. Dulepov, and N. V. Podberezskaya, *J. Struct. Chem.* **35** (1994) 236.
113. E. V. Boldyreva, S. L. Kuzmina, and H. Ahsbahs, *J. Struct. Chem.* **39** (1998) 762.
114. E. V. Boldyreva, S. L. Kuzmina, and H. Ahsbahs, *J. Struct. Chem.* **39** (1998) 343.
115. E. V. Boldyreva, D. Y. Naumov, and H. Ahsbahs, *Acta Crystallogr., Sect. B* **54** (1998) 798.
116. E. V. Boldyreva, H. Ahsbahs, D. Y. Naumov, and A. Kutoglu, *Acta Crystallogr., Sect. C* **54** (1998) 1378.
117. F. Bozoglian, M. Queirolo, and B. Sienra, *Polyhedron* **17** (1998) 3551.
118. D. Das, I. R. Laskar, A. Ghosh, A. Mondal, K. Okamoto, and N. R. Chaudhuri, *J. Chem. Soc., Dalton Trans.* (1998) 3987.
119. P. B. Novikov, D. Y. Naumov, E. V. Boldyreva, and N. V. Podberezskaya, *J. Struct. Chem.* **39** (1998) 333.
120. S. M. Jørgensen, *Z. Anorg. Allg. Chem.* **5** (1893) 169.
121. F. Basolo, J. L. Burmeister, and A. J. Poe, *J. Am. Chem. Soc.* **85** (1963) 1700.
122. J. L. Burmeister and F. Basolo, *Inorg. Chem.* **3** (1964) 1587.
123. F. Basolo, W. H. Baddley, and K. J. Weidenba, *J. Am. Chem. Soc.* **88** (1966) 1576.
124. A. Haim and N. Sutin, *J. Am. Chem. Soc.* **88** (1966) 434.
125. D. M. Goodgame and B. W. Malerbi, *Spectrochim. Acta, Part A* **24** (1968) 1254.
126. G. C. Kulasing and W. R. McWhinni, *J. Chem. Soc. A* (1968) 254.
127. T. E. Sloan and A. Wojcicki, *Inorg. Chem.* **7** (1968) 1268.
128. Gutterma.Df and H. B. Gray, *J. Am. Chem. Soc.* **91** (1969) 3105.
129. G. Beran and G. J. Palenik, *J. Chem. Soc. D* (1970) 1354.
130. L. D. Brown and D. E. Penningt, *Inorg. Chem.* **10** (1971) 2117.
131. R. C. Buckley and J. G. Wardeska, *Inorg. Chem.* **11** (1972) 1723.
132. L. A. Epps and L. G. Marzilli, *J. Chem. Soc., Chem. Commun.* (1972) 109.
133. J. L. Lauer, J. L. Burmeister, M. E. Peterkin, K. A. Johnson, and J. C. Lim, *Inorg. Chem.* **11** (1972) 907.
134. M. R. Snow and R. F. Boomsma, *Acta Crystallogr., Sect. B* **28** (1972) 1908.
135. K. A. Johnson, J. C. Lim, and J. L. Burmeister, *Inorg. Chem.* **12** (1973) 124.
136. R. L. Hassel and J. L. Burmeister, *Inorg. Chim. Acta* **8** (1974) 155.
137. A. H. Norbury and S. Raghunathan, *J. Inorg. Nucl. Chem.* **37** (1975) 2133.
138. M. Cusumano, G. Guglielmo, P. Marricchi, and V. Ricevuto, *Inorg. Chim. Acta* **30** (1978) 29.
139. D. A. Palmer, R. Vaneldik, and H. Kelm, *Inorg. Chim. Acta* **30** (1978) 83.
140. W. C. Fultz and J. L. Burmeister, *Inorg. Chim. Acta Lett.* **45** (1980) L271.
141. J. A. Kargol, K. D. Lavin, R. W. Crecely, and J. L. Burmeister, *Inorg. Chem.* **19** (1980) 1515.
142. P. E. Rutherford and D. A. Thornton, *Spectrosc. Lett.* **13** (1980) 427.
143. G. Thiele and D. Messer, *Z. Anorg. Allg. Chem.* **464** (1980) 255.
144. D. C. Calabro and J. L. Burmeister, *Inorg. Chim. Acta Lett.* **53** (1981) L47.
145. D. A. Brown, N. J. Fitzpatrick, W. K. Glass, and P. K. Sayal, *J. Organomet. Chem.* **234** (1982) C52.

146. C. T. Hunt and A. L. Balch, *Inorg. Chem.* **21** (1982) 1242.
147. C. P. Brock, J. L. Huckaby, and T. G. Attig, *Acta Crystallogr., Sect. B* **40** (1984) 595.
148. H. Ogino and H. Isago, *Chem. Lett.* (1984) 561.
149. H. H. Wei and L. Z. Ho, *Inorg. Chem.* **23** (1984) 624.
150. S. Ferrer, J. G. Haasnoot, J. Reedijk, E. Muller, M. Biaginicingi, A. M. Manottilanfredi, F. Ugozzoli, and C. Foglia, *J. Chem. Soc., Dalton Trans.* (1992) 3029.
151. M. Kakoti, S. Chaudhury, A. K. Deb, and S. Goswami, *Polyhedron* **12** (1993) 783.
152. R. D. Pike and G. B. Carpenter, *Organometallics* **12** (1993) 1416.
153. K. Eichele and R. E. Wasylishen, *Inorg. Chem.* **33** (1994) 2766.
154. A. R. Khan, S. M. Socol, D. W. Meek, and R. Yasmeen, *Inorg. Chim. Acta* **234** (1995) 109.
155. A. D. Kirk and D. M. Kneeland, *Inorg. Chem.* **34** (1995) 1536.
156. W. Preetz and M. Semrau, *Z. Anorg. Allg. Chem.* **621** (1995) 725.
157. J. U. Vogt, O. Haeckel, and W. Preetz, *Z. Anorg. Allg. Chem.* **621** (1995) 1033.
158. C. Milne and J. Milne, *Can. J. Chem.* **74** (1996) 1889.
159. M. Semrau and W. Preetz, *Z. Anorg. Allg. Chem.* **622** (1996) 1953.
160. J. U. Rohde and W. Preetz, *Z. Anorg. Allg. Chem.* **623** (1997) 1774.
161. S. Jurisson, M. M. Halihan, J. D. Lydon, C. L. Barnes, D. P. Nowotnik, and A. D. Nunn, *Inorg. Chem.* **37** (1998) 1922.
162. J. U. Rohde and W. Preetz, *Z. Anorg. Allg. Chem.* **624** (1998) 1319.
163. F. S. Nunes, P. D. L. Murta, and C. J. da Cunha, *J. Coord. Chem.* **47** (1999) 251.
164. J. Danon, R. P. A. Muniz, A. O. Caride, and I. Wolfson, *J. Mol. Struct.* **1** (1967) 127.
165. D. Gaswick and A. Haim, *J. Inorg. Nucl. Chem.* **40** (1978) 437.
166. P. Paul, R. Das, K. Nag, E. J. Gabe, and J. P. Charland, *Can. J. Chem.* **70** (1992) 2461.
167. J. E. House and N. E. Kob, *Inorg. Chem.* **32** (1993) 1053.
168. J. Berglund, R. Voigt, S. Fronaeus, and L. I. Elding, *Inorg. Chem.* **33** (1994) 3346.
169. C. A. Bignozzi, C. Chiorboli, M. T. Indelli, F. Scandola, V. Bertolasi, and G. Gilli, *J. Chem. Soc., Dalton Trans.* (1994) 2391.
170. N. Y. Zhu and H. Vahrenkamp, *Angew. Chem., Int. Ed. Engl.* **33** (1994) 2090.
171. G. A. Stark, A. M. Arif, and J. A. Gladysz, *Organometallics* **16** (1997) 2909.
172. N. Y. Zhu and H. Vahrenkamp, *Chem. Ber.* **130** (1997) 1241.
173. B. S. Lim and R. H. Holm, *Inorg. Chem.* **37** (1998) 4898.
174. E. Reguera, J. Balmaseda, G. Quintana, A. Gomez, and J. Fernandez-Bertran, *Polyhedron* **17** (1998) 2353.
175. P. Braunstein, G. E. Herberich, M. Neuschutz, and M. U. Schmidt, *J. Organomet. Chem.* **580** (1999) 66.
176. W. E. Buschmann, J. Ensling, P. Gutlich, and J. S. Miller, *Chem. Eur. J.* **5** (1999) 3019.
177. A. V. Macatangay, S. E. Mazzetto, and J. F. Endicott, *Inorg. Chem.* **38** (1999) 5091.
178. D. W. Thompson, J. R. Schoonover, T. J. Meyer, R. Argazzi, and C. A. Bignozzi, *J. Chem. Soc., Dalton Trans.* (1999) 3729.
179. G. Stochel, J. Chatlas, P. Martinez, and R. Vaneldik, *Inorg. Chem.* **31** (1992) 5480.
180. K. B. Reddy and R. Vaneldik, *Inorg. Chem.* **30** (1991) 596.
181. H. E. Toma and M. S. Takasugi, *Polyhedron* **8** (1989) 941.
182. H. E. Toma and M. S. Takasugi, *Polyhedron* **1** (1982) 429.

183. D. Pavlović, S. Ašperger, A. Hang, V. Sučić, and A. Šustra, *Acta Pharm. Jugosl.* **32** (1982) 153.
184. D. H. Macartney and A. McAuley, *J. Chem. Soc., Dalton Trans.* (1981) 1780.
185. E. B. Borghi, M. A. Blesa, P. J. Aymonino, and J. A. Olabe, *J. Inorg. Nucl. Chem.* **43** (1981) 1849.
186. D. H. Macartney and A. McAuley, *Inorg. Chem.* **20** (1981) 748.
187. R. Juretić, D. Pavlović, and S. Ašperger, *J. Chem. Soc., Dalton Trans.* (1979) 2029.
188. I. Murati, D. Pavlović, A. Šustra, and S. Ašperger, *J. Chem. Soc., Dalton Trans.* (1978) 500.
189. T. R. Sullivan, D. R. Stranks, J. Burgess, and R. I. Haines, *J. Chem. Soc., Dalton Trans.* (1977) 1460.
190. J. M. Malin, H. E. Toma, and E. Giesbrecht, *J. Chem. Educ.* **54** (1977) 385.
191. M. A. Blesa, I. A. Funai, P. J. Morando, J. A. Olabe, P. J. Aymonino, and G. Ellenrieder, *J. Chem. Soc., Dalton Trans.* (1977) 845.
192. D. Pavlović, D. Šutić, and S. Ašperger, *J. Chem. Soc., Dalton Trans.* (1976) 2406.
193. M. A. Blesa, J. A. Olabe, and P. J. Aymonino, *J. Chem. Soc., Dalton Trans.* (1976) 1196.
194. A. Žmikić, M. Pribanić, D. Pavlović, and S. Ašperger, *Croat. Chem. Acta* **47** (1975) 117.
195. Z. Bradic, M. Pribanić, and S. Ašperger, *J. Chem. Soc., Dalton Trans.* (1975) 353.
196. H. E. Toma and J. M. Malin, *Inorg. Chem.* **13** (1974) 1772.
197. Z. Bradić, D. Pavlović, I. Murati, and S. Ašperger, *J. Chem. Soc., Dalton Trans.* (1974) 344.
198. H. E. Toma and J. M. Malin, *Inorg. Chem.* **12** (1973) 2080.
199. H. E. Toma, J. M. Malin, and E. Giesbrecht, *Inorg. Chem.* **12** (1973) 2084.
200. D. Pavlović, I. Murati, and S. Ašperger, *J. Chem. Soc., Dalton Trans.* (1973) 602.
201. H. E. Toma and J. M. Malin, *Inorg. Chem.* **12** (1973) 1039.
202. H. E. Toma, A. A. Batista, and H. B. Gray, *J. Am. Chem. Soc.* **104** (1982) 7509.
203. H. E. Toma, J. M. Martins, and E. Giesbrecht, *J. Chem. Soc., Dalton Trans.* (1978) 1610.
204. A. A. Batista and H. E. Toma, *An. Acad. Bras. Cienc.* **52** (1980) 703.
205. H. E. Toma and M. M. Takayasu, *An. Acad. Bras. Cienc.* **61** (1989) 131.
206. H. E. Toma, N. M. Moroi, and N. Y. M. Iha, *An. Acad. Bras. Cienc.* **54** (1982) 315.
207. R. Walker, *J. Chem. Educ.* **57** (1980) 789.
208. A. Albert, R. Goldacre, and J. Phillips, *J. Chem. Soc.* (1948) 2240.
209. H. E. Toma, E. Giesbrecht, and R. L. E. Rojas, *Can. J. Chem.* **61** (1983) 2520.
210. R. S. Nicholson and I. Shain, *Anal. Chem.* **36** (1964) 706.
211. H. E. Toma, E. Giesbrecht, and R. L. E. Rojas, *J. Chem. Soc., Dalton Trans.* (1985) 2469.
212. R. C. Rocha, K. Araki, and H. E. Toma, *Transition Met. Chem.* **23** (1998) 13.
213. T. Matsubara and C. Creutz, *Inorg. Chem.* **18** (1979) 1956.
214. M. H. Chou, B. S. Brunschwig, C. Creutz, N. Sutin, A. Yeh, R. C. Chang, and C.-T. Lin, *Inorg. Chem.* **31** (1992) 5347.
215. B. E. Buchanan, R. Y. Wang, J. G. Vos, R. Hage, J. G. Haasnoot, and J. Reedijk, *Inorg. Chem.* **29** (1990) 3263.
216. K. D. Demadis, T. J. Meyer, and P. S. White, *Inorg. Chem.* **37** (1998) 3610.
217. K. D. Demadis, E. S. El-Samanody, T. J. Meyer, and P. S. White, *Inorg. Chem.* **37** (1998) 838.
218. W. R. Ellis and W. L. Purcell, *Inorg. Chem.* **21** (1982) 834.

219. J. H. Hall and W. L. Purcell, *Inorg. Chem.* **29** (1990) 3806.
220. S. Hubinger, J. H. Hall, and W. L. Purcell, *Inorg. Chem.* **32** (1993) 2394.
221. W. G. Jackson and S. Cortez, *Inorg. Chem.* **33** (1994) 1921.
222. W. L. Purcell, *Inorg. Chem.* **22** (1983) 1205.
223. R. R. Schmidt, G. R. Losch, and P. Fischer, *Chem. Ber.* **113** (1980) 2891.
224. W. D. Horrocks, J. N. Ishley, and R. R. Whittle, *Inorg. Chem.* **21** (1982) 3270.
225. T. G. Appleton, F. J. Pesch, M. Wienken, S. Menzer, and B. Lippert, *Inorg. Chem.* **31** (1992) 4410.
226. J. Mrozinski, M. Hvastijova, and J. Kohout, *Polyhedron* **11** (1992) 2867.
227. A. Blackman, *Reactions of Coordinated Ligands*, *Advances in Heterocyclic Chemistry*, Vol. 58, 1993, p. 123.
228. T. Ren, D. P. Bancroft, W. I. Sundquist, A. Masschelein, M. V. Keck, and S. J. Lippard, *J. Am. Chem. Soc.* **115** (1993) 11341.
229. M. Wienken, E. Zangrando, L. Randaccio, S. Menzer, and B. Lippert, *J. Chem. Soc., Dalton Trans.* (1993) 3349.
230. M. Y. Chou, S. C. Li, M. Kiso, A. Hasegawa, and Y. T. Li, *J. Biol. Chem.* **269** (1994) 18821.
231. R. Dalbies, D. Payet, and M. Leng, *Proc. Natl. Acad. Sci. USA* **91** (1994) 8147.
232. C. Colombier, B. Lippert, and M. Leng, *Nucleic Acids Res.* **24** (1996) 4519.
233. A. Guttman, F. T. A. Chen, and R. A. Evangelista, *Electrophoresis* **17** (1996) 412.
234. O. Kohle, S. Ruile, and M. Gratzel, *Inorg. Chem.* **35** (1996) 4779.
235. T. N. Parac and N. M. Kostic, *J. Am. Chem. Soc.* **118** (1996) 5946.
236. H. Sawai, J. Seki, and H. Ozaki, *J. Biomol. Struct. Dyn.* **13** (1996) 1043.
237. P. Auge and J. Kozelka, *Transition Met. Chem.* **22** (1997) 91.
238. M. Boudvillain, M. Guerin, R. Dalbies, T. SaisonBehmoaras, and M. Leng, *Biochemistry* **36** (1997) 2925.
239. Y. Chen, F. T. Lin, and R. E. Shepherd, *Inorg. Chem.* **36** (1997) 818.
240. G. Ertem and J. P. Ferris, *J. Am. Chem. Soc.* **119** (1997) 7197.
241. C. D. W. Frohling and W. S. Sheldrick, *J. Chem. Soc., Dalton Trans.* (1997) 4411.
242. S. Ruile, O. Kohle, P. Pechy, and M. Gratzel, *Inorg. Chim. Acta* **261** (1997) 129.
243. T. Taki, D. Ishikawa, H. Hamasaki, and S. Handa, *FEBS Lett.* **418** (1997) 219.
244. T. N. Parac and N. M. Kostic, *Inorg. Chem.* **37** (1998) 2141.
245. Z. J. Guo and P. J. Sadler, *Angew. Chem., Int. Ed. Engl.* **38** (1999) 1513.
246. M. B. L. Janik and B. Lippert, *J. Biol. Inorg. Chem.* **4** (1999) 645.
247. J. Kasparkova, O. Novakova, O. Vrana, N. Farrell, and V. Brabec, *Biochemistry* **38** (1999) 10997.
248. T. N. Parac, G. M. Ullmann, and N. M. Kostic, *J. Am. Chem. Soc.* **121** (1999) 3127.
249. J. Arpalahti, K. D. Klika, and S. Molander, *Eur. J. Inorg. Chem.* (2000) 1007.
250. M. J. Giraud-Panis and M. Leng, *Pharmacol. Ther.* **85** (2000) 175.
251. M. Sano and H. Taube, *Inorg. Chem.* **33** (1994) 705.
252. H. E. Toma and K. Araki, *J. Coord. Chem.* **24** (1991) 1.
253. D. O. Silva and H. E. Toma, *Can. J. Chem.* **72** (1994) 1705.
254. H. E. Toma and A. D. P. Alexiou, *Electrochim. Acta* **38** (1993) 975.
255. E. Alessio, M. Bolle, B. Milani, G. Mestroni, P. Faleschini, S. Geremia, and M. Calligaris, *Inorg. Chem.* **34** (1995) 4716.
256. M. Calligaris, P. Faleschini, F. Todone, E. Alessio, and S. Geremia, *J. Chem. Soc., Dalton Trans.* (1995) 1653.
257. E. Iengo, G. Mestroni, S. Geremia, M. Calligaris, and E. Alessio, *J. Chem. Soc., Dalton Trans.* (1999) 3361.

258. W. D. Harman, J. F. Wishart, and H. Taube, *Inorg. Chem.* **28** (1989) 2411.
259. P. A. Lay and W. D. Harman, *Adv. Inorg. Chem. Radiochem.* **37** (1991) 219.
260. H. Taube, *Pure Appl. Chem.* **63** (1991) 651.
261. L. V. Andreasen, O. Simonsen, and O. Wernberg, *Inorg. Chim. Acta* **295** (1999) 153.
262. R. L. Angel, D. P. Fairlie, and W. G. Jackson, *Inorg. Chem.* **29** (1990) 20.
263. P. M. Angus and W. G. Jackson, *Inorg. Chem.* **30** (1991) 4806.
264. P. M. Angus, W. G. Jackson, and A. M. Sargeson, *Inorg. Chem.* **32** (1993) 5285.
265. P. M. Angus, D. P. Fairlie, and W. G. Jackson, *Inorg. Chem.* **32** (1993) 450.
266. P. M. Angus and W. G. Jackson, *Inorg. Chem.* **33** (1994) 1569.
267. R. J. Balahura, *Can. J. Chem.* **52** (1974) 1762.
268. C. S. Chin, D. Chong, B. Lee, H. Jeong, G. Won, Y. Do, and Y. J. Park, *Organometallics* **19** (2000) 638.
269. N. J. Curtis, G. A. Lawrance, and A. M. Sargeson, *Aust. J. Chem.* **36** (1983) 1495.
270. N. J. Curtis, N. E. Dixon, and A. M. Sargeson, *J. Am. Chem. Soc.* **105** (1983) 5347.
271. Z. N. Darocha, G. Chiericato, and E. Tfouni, *Adv. Chem. Ser.* **253** (1997) 297.
272. N. E. Dixon, D. P. Fairlie, W. G. Jackson, and A. M. Sargeson, *Inorg. Chem.* **22** (1983) 4038.
273. D. P. Fairlie and H. Taube, *Inorg. Chem.* **24** (1985) 3199.
274. D. P. Fairlie and W. G. Jackson, *Inorg. Chim. Acta* **150** (1988) 81.
275. D. P. Fairlie, W. G. Jackson, and G. M. Mclaughlin, *Inorg. Chem.* **28** (1989) 1983.
276. D. P. Fairlie, W. G. Jackson, and K. H. Thompson, *Inorg. Chem.* **29** (1990) 3145.
277. D. P. Fairlie, T. C. Woo, W. A. Wickramasinghe, and A. C. Willis, *Inorg. Chem.* **33** (1994) 6425.
278. D. P. Fairlie, W. A. Wickramasinghe, K. A. Byriel, and H. Taube, *Inorg. Chem.* **36** (1997) 2242.
279. D. P. Fairlie, W. G. Jackson, B. W. Skelton, H. Wen, A. H. White, W. A. Wickramasinghe, T. C. Woon, and H. Taube, *Inorg. Chem.* **36** (1997) 1020.
280. D. P. Fairlie, Y. Ilan, and H. Taube, *Inorg. Chem.* **36** (1997) 1029.
281. D. P. Fairlie, M. Turner, K. A. Byriel, J. A. Mckeon, and W. G. Jackson, *Inorg. Chim. Acta* **290** (1999) 133.
282. T. Kakishita, K. Matsumura, J. Yoshitake, K. Matsumoto, and T. Kiyotsukuri, *Kobunshi Ronbunshu* **51** (1994) 59.
283. N. V. Kaminskaia and N. M. Kostic, *Inorg. Chem.* **36** (1997) 5917.
284. N. V. Kaminskaia and N. M. Kostic, *Inorg. Chem.* **37** (1998) 4302.
285. N. E. Katz and F. Fagalde, *Inorg. Chem.* **32** (1993) 5391.
286. M. Krumm, E. Zangrando, L. Randaccio, S. Menzer, and B. Lippert, *Inorg. Chem.* **32** (1993) 700.
287. U. Kunze, A. Bruns, W. Hiller, and J. Mohyla, *Chem. Ber.* **118** (1985) 227.
288. I. Lange, O. Moers, A. Blaschette, and P. G. Jones, *Z. Anorg. Allg. Chem.* **623** (1997) 1665.
289. P. Maslak, J. J. Sczepanski, and M. Parvez, *J. Am. Chem. Soc.* **113** (1991) 1062.
290. F. S. Nunes and H. Taube, *Inorg. Chem.* **33** (1994) 3111.
291. S. Ruile, O. Kohle, H. Pettersson, and M. Gratzel, *New J. Chem.* **22** (1998) 25.
292. S. A. Samath, N. Raman, K. Jeyasubramanian, and S. K. Ramalingam, *Polyhedron* **11** (1992) 33.
293. S. A. Samath and S. K. Ramalingam, *Indian J. Chem., Sect. A* **33** (1994) 779.
294. Y. Sato, M. Suzuki, T. Nirasawa, A. Suzuki, and T. Endo, *Anal. Chem.* **72** (2000) 1207.

295. M. P. Suh, K. Y. Oh, J. W. Lee, and Y. Y. Bae, *J. Am. Chem. Soc.* **118** (1996) 777.
296. A. A. Watson and D. P. Fairlie, *Inorg. Chem.* **34** (1995) 3087.
297. T. C. Woon and D. P. Fairlie, *Inorg. Chem.* **31** (1992) 4069.
298. T. C. Woon, W. A. Wickramasinghe, and D. P. Fairlie, *Inorg. Chem.* **32** (1993) 2190.
299. Y. Ilan and H. Taube, *Inorg. Chem.* **22** (1983) 1655.
300. Y. Ilan and M. Kapon, *Inorg. Chem.* **25** (1986) 2350.
301. F. N. Rein, R. C. Rocha, and H. E. Toma, *J. Coord. Chem.* **53** (2001) 99.
302. M. Noritake, K. Jitsukawa, and H. Einaga, *Ber. Bunsenges. Phys. Chem.* **96** (1992) 857.
303. Z. P. Bai, H. Einaga, and J. Hidaka, *Bull. Chem. Soc. Jpn.* **61** (1988) 1959.
304. L. Cun and R. B. Jordan, *Inorg. Chem.* **29** (1990) 2937.
305. S. Okeya, F. Egawa, Y. Nakamura, and S. Kawaguchi, *Inorg. Chim. Acta* **30** (1978) L319.
306. C. Furlani, G. Mattogno, G. Piciacchia, and B. P. Sudha, *Inorg. Chim. Acta Lett.* **44** (1980) L313.
307. M. M. Aly, *J. Coord. Chem.* **43** (1998) 89.
308. R. R. Iyengar, K. S. Bose, and C. C. Patel, *J. Inorg. Nucl. Chem.* **37** (1975) 75.
309. R. Carballo, J. S. Casas, M. S. GarciaTasende, A. Sanchez, J. Sordo, and E. M. VazquezLopez, *J. Organomet. Chem.* **525** (1996) 49.
310. A. F. Vaudo, Kantrowi.Er, and M. Z. Hoffman, *J. Am. Chem. Soc.* **93** (1971) 6698.
311. S. Yamazaki, *Polyhedron* **5** (1986) 1183.
312. Z. P. Bai, J. Hidaka, and H. Einaga, *Polyhedron* **14** (1995) 2071.
313. L. H. Piao, F. Kai, M. Hirohata, Y. Matsuoka, and H. Huang, *Polyhedron* **15** (1996) 3107.
314. M. Sado, T. Ozawa, K. Jitsukawa, and H. Einaga, *Polyhedron* **15** (1996) 103.
315. J. P. Collman and J. Y. Sun, *Inorg. Chem.* **4** (1965) 1273.
316. M. M. Aly, A. O. Baghlaf, and N. S. Ganji, *Polyhedron* **4** (1985) 1301.
317. M. M. Aly and J. J. Stephanos, *J. Mol. Struct.* **293** (1993) 75.
318. M. M. Aly and S. M. Imam, *Polyhedron* **13** (1994) 1907.
319. M. M. Aly and J. J. Stephanos, *Spectrochim. Acta, Part A* **50** (1994) 835.
320. M. M. Aly and S. M. Imam, *Monatsh. Chem.* **126** (1995) 173.
321. M. M. Aly, *Rev. Inorg. Chem.* **16** (1996) 315.
322. M. M. Aly and N. I. Al-Shatti, *Transition Met. Chem.* **23** (1998) 361.
323. M. M. Aly, *J. Coord. Chem.* **47** (1999) 505.
324. A. O. Baghlaf, M. M. Aly, and N. S. Ganji, *Polyhedron* **6** (1987) 205.
325. M. J. Lacey, J. S. Shannon, and C. G. Macdonal, *J. Chem. Soc., Dalton Trans.* (1974) 1215.
326. M. J. Lacey, C. G. Macdonald, and J. S. Shannon, *Aust. J. Chem.* **31** (1978) 1449.
327. A. S. El-Tabl and T. I. Kashar, *Pol. J. Chem.* **72** (1998) 519.
328. S. P. Kolis, J. Gonzalez, L. M. Bright, and W. D. Harman, *Organometallics* **15** (1996) 245.
329. G. B. Deacon and P. W. Felder, *J. Am. Chem. Soc.* **90** (1968) 493.
330. E. Lindner and I. P. Lorenz, *Chem. Ber.* **105** (1972) 1032.
331. S. E. Jacobson, Reichroh.P, and A. Wojcicki, *Inorg. Chem.* **12** (1973) 717.
332. E. Lindner, I. P. Lorenz, and D. Langner, *Chem. Ber.* **106** (1973) 404.
333. E. Lindner, D. W. R. Frembs, and D. Krug, *Chem. Ber.* **108** (1975) 291.
334. F. M. Akhter, M. Kojima, T. Yoshii, S. Kashino, and Y. Yoshikawa, *Chem. Lett.* (1994) 171.

335. M. Kojima, Y. Shimizu, K. Nakajima, and Y. Yoshikawa, *Bull. Chem. Soc. Jpn.* **67** (1994) 869.
336. M. Kojima, F. M. D. Akhter, K. Nakajima, and Y. Yoshikawa, *Bull. Chem. Soc. Jpn.* **69** (1996) 2889.
337. M. D. Carducci, M. R. Pressprich, and P. Coppens, *J. Am. Chem. Soc.* **119** (1997) 2669.
338. A. A. Chevalier, L. A. Gentil, and J. A. Olabe, *J. Chem. Soc., Dalton Trans.* (1991) 1959.
339. P. Coppens, D. V. Fomitchev, M. D. Carducci, and K. Culp, *J. Chem. Soc., Dalton Trans.* (1998) 865.
340. D. V. Fomitchev and P. Coppens, *Inorg. Chem.* **35** (1996) 7021.
341. J. L. Hubbard, C. R. Zoch, and W. L. Elcesser, *Inorg. Chem.* **32** (1993) 4670.
342. M. Rievaj, E. Korgova, and D. Bustin, *Bull. Soc. Chim. Belg.* **101** (1992) 671.
343. J. A. Treadway and T. J. Meyer, *Inorg. Chem.* **38** (1999) 2267.
344. U. Kolle, *Angew. Chem., Int. Ed. Engl.* **30** (1991) 956.
345. F. Baumann, A. Livoreil, W. Kaim, and J. P. Sauvage, *Chem. Commun.* (1997) 35.
946. A. Livoreil, J. P. Sauvage, N. Armaroli, V. Balzani, L. Flamigni, and B. Ventura, *J. Am. Chem. Soc.* **119** (1997) 12114.
347. J. P. Sauvage, *Acc. Chem. Res.* **31** (1998) 611.
348. L. Raehm, J. M. Kern, and J. P. Sauvage, *Chem. Eur. J.* **5** (1999) 3310.
349. J. M. Kern, L. Raehm, J. P. Sauvage, B. Divisia-Blohorn, and P. L. Vidal, *Inorg. Chem.* **39** (2000) 1555.
350. H. E. Toma, *An. Acad. Bras. Cienc.* **72** (2000) 1.

SAŽETAK

Reakcije izomerizacije veze

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Dan je pregled reakcijâ izomerizacije veze glede njihove kinetike i mehanizma, s osvrtom kako na odabrane slučajeve direktnog nastajanja tako i na nastajanja izomerne veze izazvane elektrokemijski, fotokemijski, termalno i u ovisnosti o pH.