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Linkage Isomerism in Penta-ammineruthenium(II),(III) Complexes of Benzotriazole

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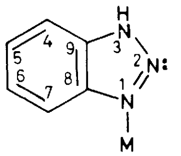
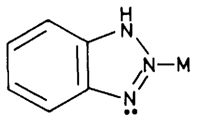
The linkage isomerism in penta-ammine(benzotriazole)ruthenium(II),(III) complexes has been investigated in aqueous solution, using spectroelectrochemistry, cyclic voltammetry, and n.m.r. (^{1}H, ^{13}C) spectroscopy. The deprotonation of the Ru^{II} complex (pK_a = 6.4) leads to a single, C_{2v} isomer which can be reversibly oxidized to Ru^{III}, with $E^\circ = -0.127$ V *versus* normal hydrogen electrode. The oxidized complex isomerizes within the time-scale of the cyclic voltammetry, forming a mixture of C_s (N^1) and C_{2v} (N^2) linkage isomers, with an equilibrium constant of 1.4 favouring the symmetric species. The analysis of the isomerization reactions in terms of a chemical–electrochemical scheme supports an intramolecular mechanism, involving π-bonded activated complexes.

The co-ordination of benzotriazole (HL) to transition-metal ions has been a subject of special interest, because of the remarkable efficiency of this ligand as a corrosion inhibitor for copper and its alloys.[1] The N-heterocyclic molecule is structurally related to the biological bases, having available more than one nitrogen atom to bind transition-metal ions. Linkage isomers are thus expected for benzotriazole complexes as shown below.



N^1 isomer



N^2 isomer

Until the last decade, kinetic and mechanistic studies of linkage isomers were mostly concerned with the nitrito-to-nitro isomerization reaction.[2–5] These studies are now appearing with increasing frequency for a variety of systems, such as ruthenium sulphoxides,[6] cobalt tetrazolates[7] and complexes with biologically important ligands, *e.g.*, imidazole,[8–10] glycine,[11–12] histidine,[13] methionine,[14,15] hypoxanthine (1,7-dihydro-6*H*-purin-6-one),[16] and uracil.[17] Recently we reported a study on the linkage isomers of benzotriazolepentacyanoferrate(II).[18] Following the rapid development of this subject, we have now investigated linkage isomerism in penta-ammineruthenium(II),(III) complexes of benzotriazole.

Experimental

Benzotriazole from Ciba was recrystallized twice from saturated aqueous solution. The complex $[Ru(NH_3)_5Cl]Cl_2$ was prepared by the method of Vogt *et al.*[19] and recrystallized several times from aqueous solutions containing 0.1 mol dm^{-3} HCl. The purity of the complex was checked spectrophotometrically.[19] The $[Ru(NH_3)_5(H_2O)]^{2+}$ ion was generated from $[Ru(NH_3)_5Cl]Cl_2$ and zinc amalgam, under an argon atmosphere. Penta-ammine(benzotriazole)ruthenium(II) was freshly prepared by reacting $[Ru(NH_3)_5(H_2O)]^{2+}$ with at least a ten-fold excess of benzotriazole, to prevent the formation of binuclear species.

Cyclic voltammetry was carried out with a Princeton Applied Research instrument, consisting of a 173 potentiostat and a 175 universal programmer. A platinum disc electrode was employed for the measurements, using the conventional Luggin capillary arrangement with the Ag/AgCl (I = 1 mol dm^{-3} KCl) reference electrode. A platinum wire was used as the auxiliary electrode. The measured potentials can be converted to the normal hydrogen electrode (n.h.e.) scale by adding 0.222 V.

The electronic spectra of the complexes were recorded on a Cary 17 spectrophotometer. For the spectroelectrochemical measurements, the PAR 173 potentiostat was used in parallel with the Cary 17 spectrophotometer. A three-electrode system was designed for a rectangular quartz cell of 0.038-cm internal optical pathlength. A platinum net, or a gold minigrid was used as a transparent working electrode, in the presence of a small Ag/AgCl reference electrode and a platinum auxiliary electrode. The experiments were carried out at 25 °C under semi-infinite diffusion conditions, as described by Kuwana and Winograd.[20]

The determination of pK_a was carried out spectrophotometrically and by cyclic voltammetry as a function of pH. Cells specially designed for the experiments were used, combining simultaneous pH measurements with absorption spectra, or cyclic voltammetry. The substitution kinetics were investigated using a Cary 14 spectrophotometer fitted with thermostatted cell compartments.

Nuclear magnetic resonance spectra were recorded on a Varian T-60 (^{1}H) or FT 80-A (^{13}C) spectrometer, at a probe temperature of 33 °C. Solutions of benzotriazole and of the corresponding ruthenium(II) complex were prepared in D_2O, under an argon atmosphere.

Results and Discussion

The $[Ru(NH_3)_5(H_2O)]^{2+}$ ion reacted with benzotriazole producing a yellow complex, $[Ru(NH_3)_5(HL)]^{2+}$, which absorbed at 410 nm ($\varepsilon = 1.32 \times 10^4$ dm^3 mol^{-1} cm^{-1}). In analogy with penta-ammineruthenium(II) complexes of aromatic N-heterocycles,[21] this band was assigned to a ruthenium-to-benzotriazole, d_π–p_{π^*} charge-transfer transition.

The formation of $[Ru(NH_3)_5(HL)]^{2+}$ followed first-order kinetics for at least three half-lives [equation (1)]. The observed

$$[Ru(NH_3)_5(H_2O)]^{2+} + HL \longrightarrow [Ru(NH_3)_5(HL)]^{2+} + H_2O \quad (1)$$

rate constants were proportional to the concentration of benzotriazole, with a second-order rate constant of 0.34 dm^3 mol^{-1} s^{-1}, $\Delta H^\ddagger$ = 70 kJ mol^{-1}, $\Delta S^\ddagger = -14$ J K^{-1} mol^{-1} at 25 °C, I = 0.20 mol dm^{-3} (sodium toluene-*p*-sulphonate). These results are comparable to those of N-heterocyclic analogues,[22] with a little more favourable $\Delta S^\ddagger$ term.

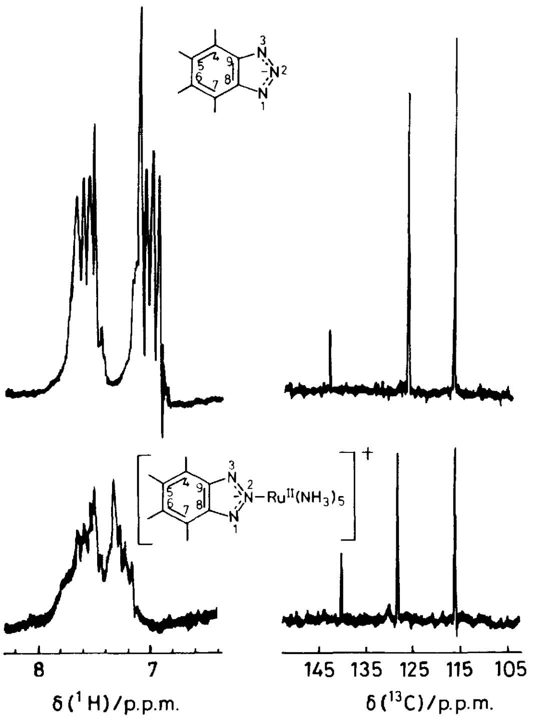


Figure 1. ^1H and ^{13}C n.m.r. spectra of L^- and $[Ru(NH_3)_5(L)]^+$ in D_2O at pD 9 and 33 °C (chemical shifts *versus* $SiMe_4$)

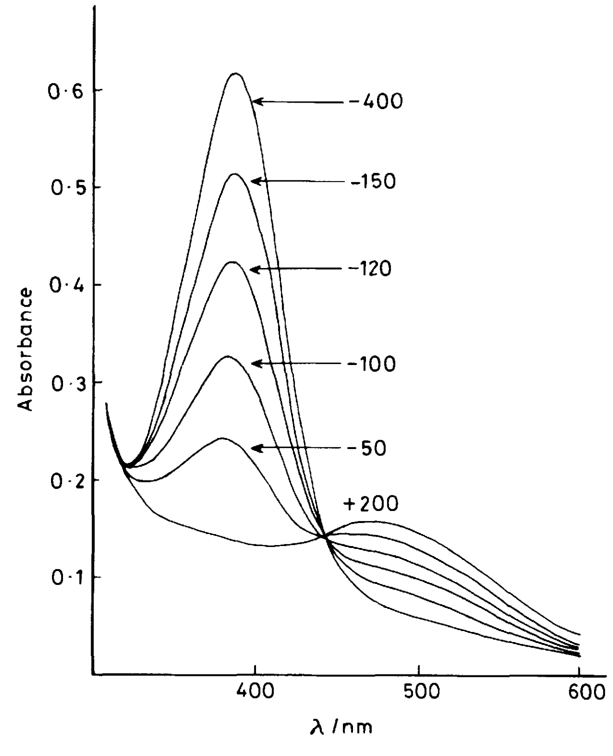


Figure 2. Spectroelectrochemistry of $[Ru(NH_3)_5(L)]^+$, starting from a potential of −400 mV *versus* Ag/AgCl, at pH 8, I = 0.5 mol dm^{-3} (KCl)

Attempts to substitute for benzotriazole in $[Ru(NH_3)_5(HL)]^{2+}$ by a ligand such as isonicotinamide were unsuccessful. The reactions proceeded very slowly, with $k_{obs.} < 10^{-7}$ s^{-1}, and led to preferential substitution of NH_3 rather than HL.

Cyclic voltammograms of $[Ru(NH_3)_5(HL)]^{2+}$ at pH 4.5 were practically reversible, with a half-wave potential of 0.030 V *versus* Ag/AgCl, and a diffusion coefficient of 3.3×10^{-6} cm^2 s^{-1}. In contrast with the analogous complex $[Fe(CN)_5(HL)]^{3-}$, no evidence of linkage isomers was observed in the cyclic voltammograms of $[Ru(NH_3)_5(HL)]^{2+}$ in mildly acidic solutions.

Above pH 7 the absorption band of $[Ru(NH_3)_5(HL)]^{2+}$ at 410 nm shifted to 385 nm ($\varepsilon = 1.05 \times 10^4$ dm^3 mol^{-1} cm^{-1}) with an isosbestic point at 387 nm. The spectral changes were ascribed to the deprotonation equilibrium shown by equation (2).

$$[Ru(NH_3)_5(HL)]^{2+} \rightleftharpoons [Ru(NH_3)_5(L)]^+ + H^+(aq.) \quad (2)$$

The pK_a of $[Ru(NH_3)_5(HL)]^{2+}$ was evaluated using equation (3), where A is the measured absorbance; A_0 and A_f are the initial and final absorbances, corresponding to the protonated and deprotonated species, respectively. Plots of equation (3) were linear, with a unit slope. The pK_a measured in this way was 6.4 ± 0.1, in comparison to 8.57 for the free ligand.[23]

$$pH = pK_a + \log[(A_0 - A)/(A - A_f)] \quad (3)$$

The deprotonation of the benzotriazole ligand led to systematic changes in the cyclic voltammograms, shifting the $E_{\frac{1}{2}}$ of the anodic peak from 0.030 V (pH 4.5) to −0.125 V (above pH 7). The pK_a of $[Ru(NH_3)_5(HL)]^{2+}$ based on cyclic voltammetry was 6.5, in excellent agreement with the spectrophotometric titration.

The ^1H and ^{13}C n.m.r. spectra of the deprotonated benzotriazole ligand and the corresponding ruthenium(II) complex are shown in Figure 1. The ^{13}C spectra consist of three peaks at 141.8, 125.5, 116.0 p.p.m., and at 138.8, 127.1, 115.3 p.p.m. associated with the $C^{8,9}$, $C^{5,6}$, and $C^{4,7}$ atoms of L^- and $[Ru(NH_3)_5(L)]^+$, respectively. The observed pattern is consistent with a C_{2v} symmetry, indicating that only the N^2 isomer is present in solution. The ^1H n.m.r. spectra consist of two groups of peaks at 7.64 and 7.08 p.p.m. for L^-, and at 7.61 and 7.32 p.p.m., for the corresponding ruthenium(II) complex. The A_2B_2 pattern corroborates the C_{2v} symmetry based on the ^{13}C data.

The spectroelectrochemistry of $[Ru(NH_3)_5(L)]^+$ is illustrated in Figure 2. The oxidation of Ru^{II} to Ru^{III} was essentially reversible, with a Nernst slope of 0.028 mV, consistent with a monoelectronic process. The ruthenium(III) product was red, with an absorption band at 480 nm, ascribed to a ligand-to-metal charge-transfer transition. The redox potential of the $[Ru(NH_3)_5(L)]^{2+/+}$ couple was −0.11 V *versus* Ag/AgCl.

Typical cyclic voltammograms of $[Ru(NH_3)_5(L)]^+$ can be seen in Figure 3. Starting from the ruthenium(II) complex at −0.4 V, a single anodic wave was observed [Figure 3(*a*)] corresponding to the oxidation of the N^2 symmetric isomer. The oxidized complex, however, leads to two cathodic waves separated by 100 mV, with their relative intensities depending upon the time-scale of the measurements as in the isomerization equilibrium reported for the benzotriazolepentacyanoferrate(II),(III) system.[18] At high potential scan rates, there is less time for the isomerization to proceed to the equilibrium position, and the intensity of the second cathodic wave becomes relatively small. At low scan rates, two cathodic waves of comparable intensity are just discernible.

For a quantitative study, the scan direction was reversed, as shown in Figure 3(*b*). Starting from the oxidized isomers, the observed pattern was quite different from that illustrated in Figure 3(*a*). At high potential scan rates, the two cathodic peaks

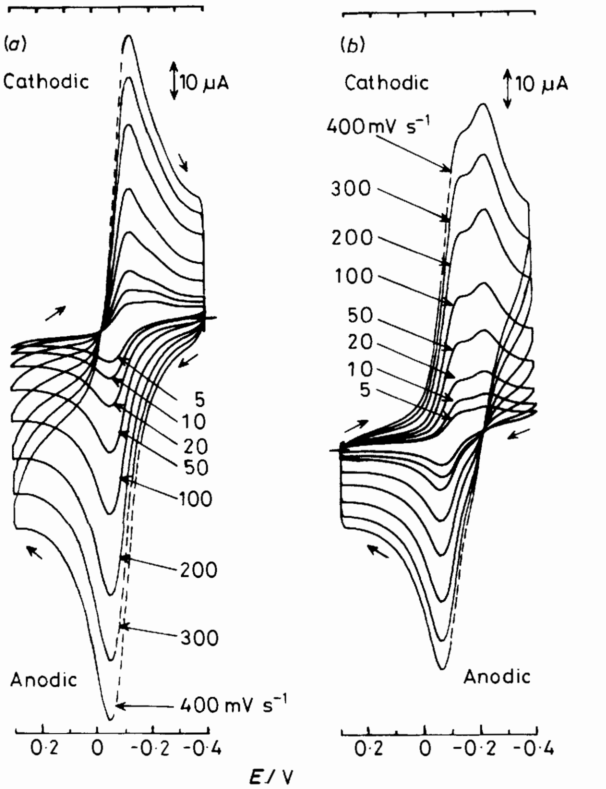


Figure 3. Cyclic voltammograms of $[Ru(NH_3)_5(L)]^+$ [2.0×10^{-3} mol dm^{-3}, pH 9, $I = 0.5$ mol dm^{-3} (KCl), 25 °C] at several potential scan rates, starting from (*a*) −400 mV and (*b*) +300 mV, after 5 min to ensure complete equilibration in solution

corresponding to the N^1 and N^2 isomers became well defined, allowing the calculation of the isomerization constant by a curve-fitting analysis, as previously described.[18] The isomerization constants K calculated in this way for the oxidized complexes were 1.40, 1.38, 1.39, and 1.45 at scan rates of 200, 300, 400, and 500 mV s^{-1}, respectively.

At low scan rates, the isomerization reaction competes with the electrochemical process, as in a typical chemical–electrochemical scheme[24] [equations (4)—(6)]. In this case, the current

$$[Ru^{III}(NH_3)_5(N^1\text{-}L)]^{2+} \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} [Ru^{III}(NH_3)_5(N^2\text{-}L)]^{2+} \quad (4)$$

$$[Ru^{III}(NH_3)_5(N^2\text{-}L)]^{2+} + e^- \longrightarrow [Ru^{II}(NH_3)_5(N^2\text{-}L)]^{+} \quad (5)$$

$$[Ru^{III}(NH_3)_5(N^1\text{-}L)]^{2+} + e^- \longrightarrow [Ru^{II}(NH_3)_5(N^1\text{-}L)]^{+} \quad (6)$$

function depends on the kinetic constants k_{12} and k_{21}, as well as on the potential scan rates a. The kinetic constants can be obtained using Nicholson and Shain's equation for a reversible chemical–electrochemical mechanism[24] equation (7), where i is

$$\frac{i_d}{i} = 1.02 + \frac{0.471}{K}\left[\frac{a}{(k_{12} + k_{21})}\right]^{\frac{1}{2}} \quad (7)$$

the observed current and i_d is the diffusion controlled current calculated from the data in the absence of chemical reactions. The diffusion current in the present case was calculated from the data obtained at high scan rates. The measured currents were multiplied by $(K + 1)/K$ in order to correct for the equilibrium concentration of the electroactive species at the applied potential.

Because the N^1 isomer is also electrochemically active, the calculations were carried out at the half-wave potential of the N^2 isomer (−0.095 V *versus* Ag/AgCl). Theoretical analysis has shown that the contribution of the N^1 isomer to the currents measured at this potential is practically zero. Typical results for $k_{12} + k_{21}$, obtained at 10, 20, 40, 50, and 100 mV s^{-1} were 0.36, 0.36, 0.32, 0.41, and 0.45 s^{-1}, with an average of 0.38 ± 0.06 s^{-1}. Similar calculations were carried out at several concentrations of the complexes, with the same results. From the values of $k_{21} + k_{12}$ and $K = k_{12}/k_{21}$ the kinetic constants k_{12} and k_{21} were calculated as 0.22 and 0.16 s^{-1}, respectively.

It is important to note in Figure 3(*b*), that at high scan rates an anodic shoulder appears at −0.17 V, with a concomitant decrease in the anodic peak at −0.06 V associated with the N^2 isomer. These two waves correspond to the N^1 and N^2 ruthenium(II) isomers under non-equilibrium conditions. By reversing the potential scan direction after a time interval varying, for instance, from 5 to 200 s, it is possible to follow the isomerization reaction as it proceeds to the equilibrium. The relaxation constant $(k_{12}' + k_{21}')$ obtained in this way was 0.04 ± 0.02 s^{-1}.

By means of the thermodynamic cycle shown below the isomerization constant (K') for the ruthenium(II) complexes was calculated as 83 ± 20. From the relaxation and equilibrium data, the kinetic constants k_{12}' and k_{21}' were evaluated as 3.9×10^{-2} and 5×10^{-4} s^{-1}, respectively.

$$\begin{tikzcd}
{[Ru^{III}(NH_3)_5(N^1\text{-}L)]^{2+}} \arrow[r, shift left, "K = 1.4"] \arrow[d, shift left] & {[Ru^{III}(NH_3)_5(N^2\text{-}L)]^{2+}} \arrow[l, shift left] \arrow[d, shift left] \\
{[Ru^{II}(NH_3)_5(N^1\text{-}L)]^{+}} \arrow[r, shift left, "K'"] \arrow[u, shift left, "-0.200\ V"] & {[Ru^{II}(NH_3)_5(N^2\text{-}L)]^{+}} \arrow[l, shift left] \arrow[u, shift left, "-0.095\ V"]
\end{tikzcd}$$

Since the ruthenium-(II) and -(III) complexes are very inert to substitution, one can conclude that the isomerization reaction proceeds by an intramolecular mechanism, *via* π-bonded activated complexes. A similar mechanism has been proposed for benzotriazolepentacyanoferrate(II)[18] and for linkage isomerization in penta-ammine(dinitrogen)ruthenium(II)[25] and $[Co^{III}(NH_3)_5(L')]^{2+}$ (HL′ = 5-methyl-2*H*-tetrazole).

The isomerization constants and activation parameters for the triazole and tetrazole complexes are given in the Table. An interesting point to note is the negative activation entropy associated with the intramolecular isomerization process. Additional cases of negative $\Delta S^{\ddagger}$ are exemplified by the linkage isomerism in ruthenium(II) sulphoxides[6] and by the nitrito-to-nitro rearrangement in rhodium(III) and iridium(III) complexes.[26] Because of the unimolecular mechanism involved in the isomerization reaction, the activated complex should be more strongly solvated than the starting complex, in order to explain the negative $\Delta S^{\ddagger}$. In this sense, the formation of non-coplanar π-bonding in the activated complex can contribute to a decrease of entropy, by liberating the ligand binding sites for hydrogen bonding or dipolar interactions with the solvent.

The site preference is another point to be analysed. CNDO/2 calculations for benzotriazole,[27] and MINDO/3 calculations for the tetrazole ligand[28] have indicated that the N^1 atom is more nucleophilic than the N^2. Thus, electronic considerations favour N^1 co-ordination of typical Lewis acids. On the other hand, steric relief can provide the required driving force for the linkage isomerization to proceed from the N^1 to the N^2 isomer, particularly in the case of the sterically hindered metal–amine complexes.

Preferential π-back-bonding stabilization of the N^2 isomer may be another important factor in Ru^{II} and Fe^{II} complexes.

Table. Isomerization constants and activation parameters for benzotriazole (HL) and 5-methyl-2*H*-tetrazole (HL′) complexes

Complex	$N^i \rightarrow N^{j\,a}$	$k_{ij}/s^{-1\,b}$	$\Delta H^‡$/kJ mol^{-1}	$\Delta S^‡$/J K^{-1} mol^{-1}	K_{ij}	Ref.
$[Ru^{II}(NH_3)_5(L)]^+$	1→2	3.9×10^{-2}			83	
	2→1	5×10^{-4}				
$[Ru^{III}(NH_3)_5(L)]^{2+}$	1→2	2.2×10^{-1}	1.5	−57	1.4	
	2→1	1.6×10^{-1}	4.7	−46		
$[Fe^{II}(CN)_5(HL)]^{3-}$	1→2	6.5×10^{-1}	9.9	−26	4.2×10^{-1}	18
	2→1	1.55	11.9	−17		
$[Fe^{III}(CN)_5(HL)]^{2-}$	1→2	4×10^{-3}			9×10^{-3}	18
	2→1	4.4×10^{-1}				
$[Co^{III}(NH_3)_5(HL')]^{3+}$	1→2	3.1×10^{-4}	15	−24	$>10^2$	7
$[Co^{III}(NH_3)_5(L')]^{2+}$	1→2	1.9×10^{-6}	26	2.5	$>10^2$	7

[a] Linkage isomers, N^1 or N^2. [b] $I = 0.10$ mol dm^{-3} (Ru, Fe) or 1.0 mol dm^{-3} (Co) (both KCl), 25 °C.

This kind of effect can be better evaluated from the ratio of the isomerization constants, K_{12}'/K_{12}, for the M^{II}—M^{III} couples, since the contribution of the steric factor is expected to cancel out or to be relatively small. In the absence of π-back-bonding, K_{12}'/K_{12} would be equal to or smaller than unity. The observed values for the Fe^{II}—Fe^{III} and Ru^{II}—Ru^{III} couples are 46 and 59, respectively, confirming the back-bonding effects expected in the Fe^{II} and Ru^{II} benzotriazole complexes. These results are also in agreement with the trends previously described for the pentacyanoferrates and ruthenium(II) ammine complexes.[29]

Acknowledgements

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