The effect of zinc(II) on the formation of 2,2'- and 2,3'-bipyridine complexes of \([\text{Ru}^{II}_2(\text{ttha})]^2-\) (ttha\(^6-\) = triethylenetetraminehexa-acetate)

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Summary

\([\text{Ru}^{II}_2(\text{ttha})(\text{H}_2\text{O})]^2-\) (ttha\(^6-\) = triethylenetetraminehexa-acetate), prepared by the reduction of the ruthenium(III) precursor, reacts with 2,2'-bipyridine (2,2'-bpy) in a multi-step fashion. The first 2,2'-bpy equivalent (1:1) adds with bidentate chelation at one ruthenium(II) site as revealed by separate ruthenium(II)/(III) waves at 0.03 and 0.54 V vs. n.h.e. A second equivalent of 2,2'-bpy (1:2) is initially stored and retained as the \([\text{Zn}(2,2'-\text{bpy})]^2+\) complex. Further addition of 2,2'-bpy initiates coordination at the second ruthenium(II) site. \([\text{Ru}_2(\text{ttha})(2,2'-\text{bpy})(\text{H}_2\text{O})]^2-\) forms a strong ion-pair with zinc(II) that is in rapid equilibrium with the \([\text{Zn}(\text{H}_2\text{O})]^2-/\ [\text{Zn}(2,2'-\text{bpy})]^2+\) pool. The solubility of the ion-pair is low. The ion-pair exhibits a shifted ruthenium(II)/(III) wave at 0.60 V. Higher amounts of 2,2'-bpy recomplex the zinc(II), solubilizing the complex and returning the \(E_{1/2}\) value to 0.54 V. Other ligands which either have a higher affinity for ruthenium(II) centres than for zinc(II) as bidentate donors (1,10-phenanthroline), or lacked the two-wave electrochemical signature of a \([\text{Ru}^{II}_2(\text{ttha})]^2-\) made by displacement of one or two \(\text{H}_2\text{O}\) molecules from \([\text{Ru}_2(\text{ttha})(\text{H}_2\text{O})]^2-\). Early work with the 1:1 complex and its apparent behaviour towards 1:2 bpy, reacting with only one mole of 2,2'-bpy per complex, led us to believe that the Ru\(^{II}\) centres become trans-bridged by one 2,2'-bpyridine. Further study has revealed that the 1:1 complex has electrochemically distinguishable Ru\(^{II}\)(bpy) and Ru\(^{III}(\text{OH}_2)\) sites, and that the presumed 1:1-bridged complexes, \([\text{Ru}_2(\text{bpy})(\text{ttha})]^2-\), lacked the two-wave electrochemical signature of a Ru\(^{II}\)(bpy)Ru\(^{III}\)(bpy)Ru\(^{III}\)(bpy)Ru\(^{III}\) sequence that would be expected for a trans-bridged complex. This contradictory chemical behaviour has now been reconciled through a role of \(\text{Zn}(\text{H}_2\text{O})^2-\), brought into solution by reduction of ruthenium(III) over Zn/Hg. Zinc(II) is a competitive complexing and storage agent for 2,2'-bipyridine that controls the molar ratio of Ru\(^{II}\):bpy in a two-step loading mechanism that produces \([\text{Ru}_2(\text{bpy})(\text{ttha})]^2-\) associated strongly with one equivalent of zinc(II). The related 2,3'-bipyridine and 4,4'-bipyridine cannot form chelates with either ruthenium(II) centres of \([\text{Ru}_2(\text{ttha})(\text{H}_2\text{O})]^2-\) or zinc(II). Therefore, \(\text{Zn}(\text{H}_2\text{O})^2-\) does not act as a competitor metal or storage complex for 2,3'-bipyridine or 4,4'-bipyridine and the presence of zinc(II) does not alter the smooth, sequential addition of 2 moles of 2,3'-bpy or 4,4'-bpy to \([\text{Ru}_2(\text{ttha})(\text{H}_2\text{O})]^2-\).

In a recent publication we showed that Cd\((\text{H}_2\text{O})^2-\) docks with pendant carboxylates of the \(\text{cis-}(R,S)-\text{Pd}((\text{eeta})]^2-\) complex as it displaces palladium(II) from eeta\(^2-\) (Ref. 13). The existence of two pendant carboxylates is an essential binding site for the entering cadmium(II), as shown in the computer-simulated structure in Figure 1.

This type of interaction is again believed to be responsible for the effect of zinc(II) on the formation of \([\text{Ru}_2(\text{bpy})(\text{ttha})]^2-\). The bidentate nature of 2,2'-bpy requires displacement of one in-plane glycinato donor per ruthenium(II) site. These charged carboxylates are then available to attract \(\text{Zn}(\text{H}_2\text{O})^2-\), forming a tight ion-pair of overall zero charge. The zinc(II) must be present at the end of a two-rod-like repeat unit associated with a carboxylate and be ready to stack as (2',2') pairs in the solid state. Indeed, the ion-paired species has low-solubility, which hampered characterization methods.

Introduction

Ruthenium polyaminocarboxylates, Ru(pacs), have many potential uses in catalysis and medicine\(^{1-3}\). Ru(pacs), such as \([\text{Ru}^{III}(\text{edtaH})(\text{H}_2\text{O})]\), have an important position among water-soluble homogeneous catalysts\(^4\) for commercial processes, including olefin hydrogenations\(^5\), hydroformylation\(^6\), carbonylation\(^7\), O\(_2\)-activated oxidations of olefins, phosphines, amines and sulfoxides\(^8\), and the reduction of NO\(^9\), \([\text{Ru}_2(\text{ttha})-(\text{H}_2\text{O})]^2-\) is a catalyst precursor for the electrochemical oxidation of NO to HNO\(_2\)\(^{10}\). \([\text{Ru}_2(\text{ttha})(\text{H}_2\text{O})]^2-\) forms a bridged complex with pyrimidine\(^{11}\) and hydroxide\(^{12}\). The hydroxo/oxo-bridged complexes allow for a complete series of mixed oxidation state ions with oxidation assignments of [II,II], [II,III], [III,III], and [III,IV] having been characterized\(^{12}\).

The relationship between catalytic redox behaviour and the mixed-oxidation state complexes led us to take an interest in the 2,2'-bipyridine complex of \([\text{Ru}^{II}_2(\text{ttha})]^2-\) made by displacement of one or two \(\text{H}_2\text{O}\) molecules from \([\text{Ru}_2(\text{ttha})(\text{H}_2\text{O})]^2-\). Early work with the 1:1 complex and its apparent behaviour towards 1:2 bpy, reacting with only one mole of 2,2'-bpy per complex, led us to believe that the Ru\(^{II}\) centres become trans-bridged by one 2,2'-bpyridine. Further study has revealed that the 1:1 complex has electrochemically distinguishable Ru\(^{II}\)(bpy) and Ru\(^{III}(\text{OH}_2)\) sites, and that the presumed 1:1-bridged complexes, \([\text{Ru}_2(\text{bpy})(\text{ttha})]^2-\), lacked the two-wave electrochemical signature of a Ru\(^{II}\)(bpy)Ru\(^{III}\)(bpy)Ru\(^{III}\)(bpy)Ru\(^{III}\) sequence that would be expected for a trans-bridged complex. This contradictory chemical behaviour has now been reconciled through a role of \(\text{Zn}(\text{H}_2\text{O})^2-\), brought into solution by reduction of ruthenium(III) over Zn/Hg. Zinc(II) is a competitive complexing and storage agent for 2,2'-bipyridine that controls the molar ratio of Ru\(^{II}\):bpy in a two-step loading mechanism that produces \([\text{Ru}_2(\text{bpy})(\text{ttha})]^2-\) associated strongly with one equivalent of zinc(II). The related 2,3'-bipyridine and 4,4'-bipyridine cannot form chelates with either ruthenium(II) centres of \([\text{Ru}_2(\text{ttha})(\text{H}_2\text{O})]^2-\) or zinc(II). Therefore, \(\text{Zn}(\text{H}_2\text{O})^2-\) does not act as a competitor metal or storage complex for 2,3'-bipyridine or 4,4'-bipyridine and the presence of zinc(II) does not alter the smooth, sequential addition of 2 moles of 2,3'-bpy or 4,4'-bpy to \([\text{Ru}_2(\text{ttha})(\text{H}_2\text{O})]^2-\).

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RuII and RuIII complexes

Na[RuII(hedta)(OH2)] and Na[RuIII(hedta)Cl] (1) were available from prior studies. Na2[RuII(ttha)(H2O)]2 (2) was available from prior work, however, it was not observed that the sample had undergone air-oxidation to Na2[RuII(ttha)(OH2)]. This was not deemed to be a problem as reduction of the sample over Zn/Hg in acidic solution (pH ~ 3) afforded the [RuII(ttha)(OH2)]2− complex, which reacted with 2-Mepz or other η1 acceptor ligands to give the requisite amount of absorbance changes and the same RuII products as the original Na2[RuII(ttha)(H2O)]2 starting material. Samples were routinely reduced over Zn/Hg under Ar to produce [RuII(ttha)(H2O)]2− and [Ru(hedta)H2O]− reagents to remove traces of RuIII from the Na[RuII(hedta)(H2O)] starting materials. Air-sensitive solutions were handled by gas-tight syringe techniques or by passage of solutions through teflon surgical tubing and stainless steel needles between reaction flasks and Ar-purged and sealed u.v.-vis. cells or n.m.r. tubes. An anion exchange study on the [RuII(ttha)(bpy)](H2O)2− and [RuIII(bpy)](thta)2− species identified them as 2− ions, which moved on AG-4X anion exchange resin with 0.50 m NaCl. This ruled out cross-linked polymeric units with charges as multiples of 2− for dimers, trimers, etc. of the main binuclear [RuII(ttha)2]2− units.

Instrumentation

U.v.-vis. spectra were recorded on a Varian-Cary 118C spectrophotometer in Ar-purged 1.0, 2.0 and 0.20 cm quartz cells. Adjustments to the pH were made on the ruthenium complexes under Ar by means of addition of standard NaOH or HCl via a microsyringe. The pH was recorded with a Fisher Accumet digital pH meter standardized against commercial buffers prior to mounting of the minicomination glass electrode through a rubber septum port on the reaction vessel used to prepare the complexes. Aliquots were removed periodically to obtain spectra.

1H-n.m.r. spectra were obtained on a Bruker AFS/00 MHz n.m.r. operating at 300.13 MHz with a 70.46 kG field. Shifts in the spectra were referenced against either HOD or internal DSS. I.r. spectra were recorded on an IBM IR 30 FTIR using 64 to 100 scans for signal averaging. Complexes were isolated from solution upon the addition of ethanol to induce precipitation of the Na[Ru(hedta)L] and Na2[RuII(ttha)L] solids. After filtration and drying in a vacuum oven, ground samples of these salts were pressed into KBr pellets at 9 tons pressure. The i.r. spectrum of Na[RuII(ttha)(2,2′-bpy)(H2O)] and Zn[RuII(ttha)(2,2′-bpy)] showed no evidence of a free carboxylate functionality [ν(CO2M) = 1620 cm−1]. The 1,10-phenanthroline complex at a 1:1 ratio with (2) also did not exhibit an obvious free carboxylate [ν(CO2M) = 1620 cm−1] even though bidentate chelation induces loss of a glycinato donor.

Na[RuII(hedta)(1,10-phen)] has a carboxylate stretch at 1607 cm−1 with a slight shoulder feature at 1590 cm−1, indicative of one pendant carboxylate and ca. 1600 cm−1 in the carboxylate region for a bidentately coordinated ruthenium(II) complex. Other Na[RuII(hedta)L] complexes gave related carboxylate bands at 1642 cm−1, L = H2O; 1609 cm−1, L = 2,2′-bpy; and 1617 cm−1, L = 2,2′-Me2bpy.

Electrochemical methods

Electrochemical measurements were made in the standard three-electrode configuration with glassy carbon as the working electrode. Measurements were performed on an IMB EC-225 analyser in both the cyclic voltammetry (c.v.) and different pulse polarography (d.p.p) modes. Measurements were made at 22 °C in 0.10 m NaCl. A 50 mVs scan rate was used for c.v. and 40 mVs for scanning of the d.p.p. waves along with a 50 mV stepping voltage. The instrument was calibrated using the ruthenium(II)/(III) waves of Ru(NH3)62+/3+ and [Ru(hedta)(H2O)]0+/1+ couples.

Results and discussion

[RuII(ttha)(H2O)]2− reaction with 2,2′-bipyridine

A sample of [RuII(ttha)(H2O)]2− (2) was prepared in solution under Ar as described in the Experimental se-