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A Soluble 5-Phenyltetrazolate-bridged Rhodium(III) Oligomer

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Recent investigations have shown that 5-phenyltetrazolate (T^-)** and *para*-substituted 5-phenyltetrazolates react with Fe^{2+}, Co^{2+} and Ni^{2+} to form soluble, high molecular weight polymers with rod-like structures [1–4]. The general formula for the Fe^{2+} and Ni^{2+} species is $[ML_3^-]_n$; that for the Co^{2+} species is $[CoL_2(H_2O)(OH)^-]_n$ (L = tetrazolate ligand). In the Fe^{2+} and Ni^{2+} polymers each tetrazolate bonds to adjacent metal ions through N(2) and N(3) to form three bridges per metal. In the Co^{2+} polymer there are two such bridges and it has been proposed that hydrogen bonding between OH^- and H_2O on adjacent monomer units results in a third bridge.

Since only first transition series metals have been shown to form these species, it was of interest to determine if heavier metals would also react with tetrazolates to form soluble polymers. We now wish to report that Rh^{3+} and T^- form a relatively short-chain species with a structure roughly analogous to that of the Co^{2+}/T^- complex and that its monomer unit, unlike those of the other members of this family, is cationic. The fact that Rh^{3+} forms an oligomeric tetrazolate complex suggests that the essential electronic factors which lead to long-chain polymer formation with first transition series metals are also present in this system and that other factors limit its length.

Experimental

Synthesis of 5-Phenyltetrazole and Sodium 5-Phenyltetrazolate

5-Phenyltetrazole [5] and sodium 5-phenyltetrazolate [2] were prepared as previously described.

Synthesis of Bis-μ-5-phenyltetrazolatodiaaquorhodium(III)

When aqueous solutions of NaT and $Rh(NO_3)_3 \cdot 2H_2O$ (from Alfa/Ventron Inorganics or Fluka Chemical Corporation) were mixed, UV–Vis absorption spectra indicated the formation of a new soluble species within minutes. When the Rh^{3+} concentration was 1.0×10^{-4} M or lower, the compound remained soluble for several days; at higher concentrations yellow precipitates formed within hours. The precipitates were non-stoichiometric and had various compositions with T^- to Rh^{3+} ratios ranging from less than one to two, suggesting that the solids are mixtures of oxy/hydroxy/T^- Rh^{3+} species.

Physical Methods

UV–Vis spectra were recorded on a Beckman Model M-VI or a Varian Cary Model 2300 spectrophotometer. Absorption spectra of Rh^{3+}/T^- solutions were recorded against reference solutions containing T^- (or Rh^{3+}) at the same concentration initially present in the sample solution. Absorbance readings reported for the Rh^{3+}/T^- species were determined by subtracting the absorbance of a corresponding Rh^{3+} (or T^-) solution from the recorded spectrum.

Osmotic pressure [2] and electrophoresis [4] measurements were made as previously described. Electrophoresis gels were 1% agarose, 0.4% Na_2SO_4 and 1×10^{-3} M in T^-. Solutions containing the Rh^{3+}/T^- species which were 1×10^{-4} M in metal and 1×10^{-3} M in T^- were run for 30 min at 0 °C and 80 V, during which time the currents rose from 85 to 140 mA. After a gel was allowed to dehydrate in air, the position of the band containing the Rh^{3+}/T^- species was detected visually. Positions were confirmed by dissolving fractions of wet gel in concentrated HCl and measuring the Rh concentration using a Perkin-Elmer Model 2380 atomic absorption spectrophotometer.

Titrations were carried out using a Leeds and Northrup Model 7047 or an Orion Model 611 pH meter. Corrections for solvent acidity were made by subtracting the amount of base required to titrate a matching NaT solution to the equivalence point for the sample solution. The concentrations used in the osmotic pressure and titration experiments were the highest possible consistent with ensuring that no precipitation occurred during the course of the experiment.

Mean values of experimentally determined quantities are reported; their uncertainties are expressed as 95% confidence limits. The number of independent measurements, *N*, is given in parentheses.

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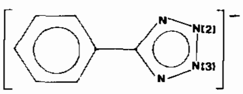
**The structure and numbering convention for 5-phenyltetrazolate is



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Results and Discussion

The structure of the Rh^{3+}/T^- monomer unit was determined using UV–Vis spectrophotometry to ascertain the coordination number of the metal and the T^- to Rh^{3+} ratio, electrophoretic measurements to ascertain the charge on the species, and potentiometric titrations to ascertain the number of coordinated waters per metal ion. Osmotic pressure measurements were used to determine the number of metal ions per molecule.

UV–Vis spectra of solutions containing the Rh^{3+}/T^- species exhibited absorbance 'shoulders' at 272 nm ($\epsilon = 260$ M^{-1} cm^{-1}) and 282 nm ($\epsilon = 160$ M^{-1} cm^{-1}) which are typical of spectra of octahedral Rh(III) complexes [6]. Limiting absorbance values for the complex were found to occur at a T^- to Rh^{3+} ratio of six. Continuous variation studies at 282 nm using solutions in which the total molarity of ligand and metal was 1.25×10^{-3} M gave maximum absorbances at a mole fraction Rh^{3+} of 0.33 ± 0.02 ($N = 3$), which corresponds to a T^- to Rh^{3+} ratio of 2.0 ± 0.2.

Electrophoresis of solutions which were 1.0×10^{-4} M in Rh^{3+} and 1.0×10^{-3} M in T^- gave single bands which moved toward the negative electrode, showing the Rh^{3+}/T^- species present are cationic.

Titration of 1.0×10^{-4} M $Rh^{3+}/1.0 \times 10^{-3}$ M T^- solutions 1 to 2 h after preparation gave single equivalence points at pH 7.7, corresponding to an OH^- to Rh^{3+} ratio of 2.08 ± 0.04 ($N = 37$), which indicates there are more than two water molecules per Rh^{3+} ion in the complex.

Osmotic pressure measurements made on 5.0×10^{-5} M $Rh^{3+}/5.0 \times 10^{-4}$ M T^- solutions gave a net capillary rise of 0.14 ± 0.06 cm ($N = 3$), which corresponds to 9 ± 4 rhodium ions per molecule.

The only structure consistent with all of the data is an oligomeric species with a monomer unit $RhT_2(H_2O)_2^+$ in which bidentate T^- forms two bridges per monomer unit between adjacent metal ions. In addition, hydrogen bonding between coordinated water molecules on neighboring metal ions could result in a third bridge.

The fact that the experimental H_2O to Rh^{3+} ratio is greater than two most likely arises from stoichiometric 'end effects', which are negligible in long-chain species but significant here because of the relatively short length of the species. Specifically, an exact Rh^{3+}:T^-:H_2O ratio of 1:2:2 would require that there be, in addition to the bidentate bridging T^- ligands and water molecules in the 'middle' of the molecule, a total of two monodentate T^- ligands and two unoccupied sites at the ends of the molecule. However, unoccupied end sites are unlikely since Rh^{3+} is usually octahedrally coordinated [7].

The only combination of end-site occupancy and molecular length which is consistent with the experimental mean values of both the T^- to Rh^{3+} and H_2O to Rh^{3+} ratios corresponds to a molecule containing 25 monomer units and having two water molecules and two T^- ligands occupying the four end sites. If the uncertainty in the H_2O to Rh^{3+} ratio is considered, a range of 17 to 50 monomer units per molecule results. Extreme upper and lower limits for the number of monomer units per molecule may be estimated by considering the range of end-site occupancy consistent with the uncertainty limits for the H_2O to Rh^{3+} and T^- to Rh^{3+} ratios. Specifically, a lower limit of eight monomers per molecule is found if the H_2O to Rh^{3+} ratio is 2.12 and one H_2O and three T^- ligands occupy the four end sites. An upper limit of 100 monomers per molecule is found if the H_2O to Rh^{3+} ratio is 2.04 and four water molecules occupy the end sites. The T^- to Rh^{3+} ratios which correspond to the lower and upper limits are 2.12 and 1.98, respectively; both are within the experimental uncertainty limits for this ratio.

While the actual number of each type of ligand occupying the end sites of the molecule is not known, both the titration data and the osmotic pressure results clearly indicate that the $[RhT_2(H_2O)_2^+]_n$ species is a relatively short-chain molecule. The fact that the molecular length values given by the osmotic pressure measurements (made at 5.0×10^{-5} Rh^{3+}) are lower than those derived from the titration studies (made at 1.0×10^{-4} Rh^{3+}) indicates that the Rh^{3+}/T^- system is 'open-ended' like the first transition series species, for which length was found to be concentration dependent [4]. It thus appears that the bonding elements necessary for the formation of long-chain species are present in the Rh^{3+}/T^- system and that other characteristics—most likely its lower solubility, its positive charge and/or the fact that it contains a 4d metal—limit its length.

In an effort to determine the effect of the lower solubility on chain length, solutions of Ni^{2+} and T^- were titrated under the same conditions used for the Rh^{3+}/T^- studies*. The Ni^{2+}/T^- solutions exhibited single equivalence points at pH 7.7, corresponding to an H_2O to Ni^{2+} ratio of 0.14 ± 0.04 ($N = 3$). Assuming that the species present is $[NiT_3^-]_n$ and that the three remaining end coordination sites in this molecule are filled with H_2O, the experimental H_2O to Ni^{2+} ratio corresponds to an average of 21 (range 17–30) monomers per molecule, which is similar to that obtained for the Rh^{3+}/T^- species at the same concentration. Since Ni^{2+} forms long-chain tetrazolate complexes at higher concentrations, it is clear that the limited solubility of the Rh^{3+}/T^- species alone could explain its shorter chain length.

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*The Ni^{2+}/T^- system was used because Co^{2+} and T^- do not react appreciably at concentrations below 1×10^{-3} M Co^{2+} [2].

We are now in the process of preparing tetrazolate complexes of other 4d and 5d metals to determine if metal size or charge on the monomer also influence the length of these species.

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