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Soluble, Polymeric 5-(*p*-Nitrophenyl)- and 5-(*p*-Methylphenyl)tetrazolate Complexes of Co(II) and Ni(II)

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Abstract

The synthesis and characterization of three additional members of a unique family of soluble, rigid rod-like polymers containing first transition series metals and 5-phenyltetrazolate (T^-) or substituted 5-phenyltetrazolates (RT^-) are reported. Viscometric, spectrophotometric, titrimetric, electrophoretic and heat sensitivity data indicate that the formulas of the new species are $[Ni(p\text{-}NO_2T)_3^-]_n$, $[Ni(p\text{-}CH_3T)_3^-]_n$ and $[Co(p\text{-}CH_3T)_2(H_2O)(OH)^-]_n$. The fact that Cu^{2+} does not form such polymers is also reported. Electrophoretic measurements show that the Co^{2+}/T^- polymer is anionic rather than neutral as previously proposed. A systematic viscosity study of all the polymers indicates that their intrinsic viscosities are comparable. The results suggest that triple bridging between metal ions is characteristic of these complexes.

Introduction

To date the only reported examples of soluble, rod-like polymeric transition metal complexes are members of the family of compounds containing 5-phenyltetrazolate (hereinafter T^-) (Fig. 1) or one of its derivatives (RT^-) and metal ions of the first transition series. The species which have been reported are $[NiT_3^-]_n$ [1], $[CoT_2(H_2O)_2]_n$ [2], $[FeT_3^-]_n$ and $[Fe(p\text{-}CH_3T)_3^-]_n$ [3]. 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 ion. In the Co^{2+} polymer there are two such bridges and it has been proposed that pairs of coordinated waters on adjacent metal ions hydrogen bond to form a third bridge. In addition, it appears that polymers do not form first row transition metal ions with fewer than six d electrons, from tetrazolates without the phenyl group, nor from $p\text{-}NO_2T^-$ and Fe^{2+} or Co^{2+}. Consideration of these results has led to the suggestion that ligand π^*–metal t_{2g} orbital overlap and the presence of some minimum electron density in the resulting π system play an important role in stabilizing these long-chain polymeric complexes [3].

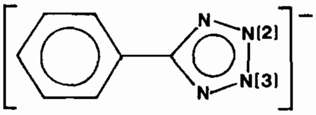

Fig. 1. The structure and numbering convention for 5-phenyltetrazolate.

We now wish to report the synthesis and characterization of three additional members of this family of compounds – those containing Co^{2+} and $p\text{-}CH_3T^-$, Ni^{2+} and $p\text{-}CH_3T^-$, and Ni^{2+} and $p\text{-}NO_2T^-$ – and the fact that Cu^{2+} does not form soluble compounds with any of the 5-phenyltetrazolates. A systematic viscosity study of the seven soluble polymers is also reported. The results provide further evidence that some minimum electron density is needed if these polymers are to form, show that the Co^{2+} polymers are negatively charged, rather than neutral as previously proposed, and suggest that triple bridging is characteristic of the species.

Experimental

Preparation of Tetrazoles and Tetrazolates

5-Phenyltetrazole, 5-(*p*-nitrophenyl)tetrazole, and 5-(*p*-methylphenyl)tetrazole were synthesized according to procedures reported in the literature [4]. The sodium salts of these compounds were prepared as previously described [2].

Preparation of Co(II) 5-(p-Methylphenyl)tetrazolate Complexes

When aqueous solutions of $Co(NO_3)_2 \cdot 6H_2O$ and $Na(p\text{-}CH_3T)$ were mixed to yield solutions in which

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the Co^{2+} concentration ranged from 0.001 to 0.01 M and the p-CH_3T^- to Co^{2+} ratio was ten, pink precipitates formed immediately. *Anal.* Calc. for $Co(p$-$CH_3T)_2 \cdot 3H_2O$: C, 44.55; H, 4.64; N, 26.00; Co, 13.66. Found: C, 44.64; H, 4.73; N, 25.99; Co, 12.72%. (All analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.) When the Co^{2+} concentration was at least 0.005 M and the temperature of the mixture was kept below 10 °C, the precipitates dissolved in one to two days, yielding viscous, yellow solutions. When these solutions were heated above 10 °C, pink precipitates again formed. *Anal.* Found for $Co(p$-$CH_3T)_2 \cdot 3H_2O$: C, 43.69; H, 4.78; N, 25.83; Co, 14.71%. Addition of methanol to the solutions also resulted in the formation of pink precipitates. *Anal.* Calc. for $Co(p$-$CH_3T)_2 \cdot 1.5H_2O$: C, 47.52; H, 4.21; N, 27.72; Co, 14.60. Found: C, 47.63; H, 4.56; N, 27.82; Co, 13.07%.

Preparation of Ni(II) 5-(p-Nitrophenyl)- and 5-(p-Methylphenyl)tetrazolate Complexes

When aqueous solutions of $Ni(NO_3)_2 \cdot 6H_2O$ and $Na(p$-$NO_2T)$ were mixed to yield solutions in which the Ni^{2+} concentration ranged from 0.001 to 0.01 M and the p-NO_2T^- to Ni^{2+} ratio was ten, pale violet precipitates formed immediately. *Anal.* Calc. for $Ni(p$-$NO_2T)_2 \cdot 4H_2O$: C, 32.90; H, 3.13; N, 27.41; Ni, 11.49. Found: C, 32.87, H, 3.21; N, 27.33; Ni, 10.99%. When the Ni^{2+} concentration was less than 0.005 M, the precipitates dissolved completely in one to two days, yielding viscous, yellow–orange solutions. An orange precipitate of $NaNi(p$-$NO_2T)_3 \cdot 5H_2O$ was isolated from one of these solutions by slowly evaporating the solution to dryness and washing the residue with large amounts of water and methanol. *Anal.* Calc. for $NaNi(p$-$NO_2T)_3 \cdot 5H_2O$: Ni, 7.91; C, 33.98; N, 28.31; H, 2.97; Na, 3.10. Found: Ni, 7.04; C, 34.24; Ni, 28.25; H, 3.10; Na, 3.27%. When the yellow–orange solutions were refluxed at 100 °C for several hours, pale violet precipitates again formed. *Anal.* Calc. for $Ni(p$-$NO_2T)_2 \cdot 3H_2O$: C, 34.10; H, 2.84; N, 28.41; Ni, 11.91. Found: C, 34.18; H, 2.71; N, 28.01; Ni, 10.82%.

When aqueous solutions of $Ni(NO_3)_2 \cdot 6H_2O$ and $Na(p$-$CH_3T)$ were mixed to yield solutions in which the Ni^{2+} concentration ranged from 0.001 to 0.01 M and the p-CH_3T^- to Ni^{2+} ratio was ten, blue precipitates formed immediately. *Anal.* Calc. for $Ni(p$-$CH_3T)_2 \cdot 4H_2O$: C, 42.79; H, 4.00; N, 24.96; Ni, 12.92. Found: C, 42.68; H, 5.06; N, 24.99; Ni, 12.60%. After several weeks, the precipitate dissolved only in the 0.001 M Ni^{2+}/0.01 M p-CH_3T^- mixture, yielding a viscous, pink–purple solution. When this solution was heated above 80 °C, a blue precipitate formed. *Anal.* Calc. for $Ni(p$-$CH_3T)_2 \cdot 5H_2O$: C, 41.13; H, 5.14; N, 24.00; Ni, 12.28. Found: C, 40.48; H, 5.19; N, 24.16; Ni, 12.28%.

Preparation of Cu(II) 5-Phenyl-, 5-(p-Nitrophenyl)- and 5-(p-Methylphenyl)tetrazolate Complexes

When aqueous solutions of $Cu(NO_3)_2 \cdot 3H_2O$ and NaT were mixed to yield solutions in which the Cu^{2+} concentration ranged from 0.001 to 0.01 M and the T^- to Cu^{2+} ratio was ten or more, granular blue–gray precipitates formed. *Anal.* Calc. for $CuT_2 \cdot 2H_2O$: C, 43.13; N, 28.74; H, 3.62; Cu, 16.30. Found: C, 42.78; N, 28.43; H, 3.55; Cu, 17.25% [5]. When aqueous solutions of Cu^{2+} and p-NO_2T^- were mixed under the same conditions, granular blue precipitates formed initially but, within minutes, they became blue–green and gelatinous. The latter analysed as $Cu(p$-$NO_2T)_2 \cdot 9H_2O$. *Anal.* Calc. for $Cu(p$-$NO_2T)_2 \cdot 9H_2O$: C, 27.75; N, 23.12; H, 4.33; Cu, 10.49. Found: C, 27.70; N, 23.09; H, 4.07; Cu, 10.52%. When aqueous solutions of Cu^{2+} and p-CH_3T^- were mixed under these conditions, granular blue–violet precipitates formed. *Anal.* Calc. for $Cu(p$-$CH_3T)_2 \cdot 1.5H_2O$: C, 47.00; N, 27.40; H, 4.19; Cu, 15.54. Found: C, 46.90; N, 27.80; H, 4.02; Cu, 16.47%. None of the precipitates dissolved in the presence of excess ligand.

Physical Methods

UV–Vis spectra were recorded using a Beckman M-VI spectrophotometer. Potentiometric titrations were made with an Orion Model 611 pH meter. Viscosities were measured at 10 °C using a modified Ostwald-Fenske viscometer with a water flow time of 339 s.

Electrophoresis measurements were made using a Blaircraft minicell gel electrophoresis apparatus and a Heathkit Model IP-17 regulated power supply. The gels were 1% agarose and 0.05 M in ligand; the agarose was molecular biology grade from International Biotechnologies Inc., New Haven, Conn. A 0.2 M NH_4Cl/0.2 M NH_3 buffer was used in the electrode compartments. Polymer solutions, which were 0.005 M in metal and 0.05 M in ligand (unless otherwise specified), were run for 30 min at 0 °C and 80 V, during which time the currents rose from approximately 50 to 150 mA. The bands containing the colored polymers were observed directly after the gel was allowed to partially dehydrate in air to concentrate the samples.

Results and Discussion

The qualitative behavior of solutions containing the Co^{2+}/p-CH_3T^-, Ni^{2+}/p-NO_2T^- and Ni^{2+}/p-CH_3T^- species reported here was similar to that observed for the Co^{2+}/T^-, Ni^{2+}/T^-, Fe^{2+}/T^-, and Fe^{2+}/p-CH_3T^- species reported earlier. To demonstrate that the three new soluble species are also polymeric with structures similar to those of the previously reported compounds, systematic viscosity measurements were made on all seven systems. Except for the $Ni^{2+}/p\text{-}CH_3T^-$ system, stock solutions were 0.004 M in metal and 0.08 M in ligand and were stored at 2–4 °C. Because of solubility problems, the solution used for the $Ni^{2+}/p\text{-}CH_3T^-$ study was approximately 0.0036 M in Ni^{2+} and 0.079 M in $p\text{-}CH_3T^-$. It was prepared by stirring a mixture which was initially 0.004 M in Ni^{2+} and 0.08 M in $p\text{-}CH_3T^-$ at room temperature for ten weeks, after which time centrifugation produced a viscous, pink solution and some solid $Ni(p\text{-}CH_3T)_2$. The latter was washed, dried and weighed in order to determine the concentration of the polymer solution. At various intervals after preparation the intrinsic viscosity, $[\eta]$, of each polymer was determined as previously described [2].

All of the Fe^{2+} and Co^{2+} polymers achieved limiting (equilibrium) values of $[\eta]$ after four weeks or less. Limiting $[\eta]$ values for the T^- and $p\text{-}CH_3T^-$ compounds of Fe^{2+} were 5000 and 2500 ml g^{-1}; for the T^- and $p\text{-}CH_3T^-$ compounds of Co^{2+} the values were 6000 and 4000 ml g^{-1}, respectively. The intrinsic viscosities of the Ni^{2+} polymers continued to increase for at least thirty weeks. $[\eta]$ values for the $(NiT_3^-)_n$ and $[Ni(p\text{-}NO_2T)_3^-]_n$ species were 2500 and 4000 ml g^{-1} after four weeks, 4000 and 5000 ml g^{-1} after twelve weeks and 6500 and 8000 ml g^{-1} after thirty weeks, respectively. Measurements made using the 0.0036 M Ni^{2+}/0.079 M $p\text{-}CH_3T^-$ solution described above gave an $[\eta]$ value for the $[Ni(p\text{-}CH_3T)_3^-]_n$ polymer of 5500 ml g^{-1} after twelve weeks. The very high $[\eta]$ values obtained for the three new species are comparable to those of the previously reported compounds and strongly suggest that they are also rod-like polymers.

In order to further characterize these polymers and determine their respective monomer units, spectrophotometric, titrimetric, electrophoretic and heat sensitivity measurements were made.

Solutions containing the yellow, polymeric $Co^{2+}/p\text{-}CH_3T^-$ species have visible spectra with a λ_{max} at 450 nm ($\epsilon = 35$ l mol^{-1} cm^{-1}) which indicates the coordination around the Co^{2+} ion is octahedral [6a]. Titration of a 0.005 M Co^{2+}/0.05 M $p\text{-}CH_3T^-$ solution with 0.01 M NaOH gave a single equivalence point, at pH 10.4, corresponding to an OH^- to Co^{2+} ratio of 1.0 (with a precipitate forming before the equivalence point was reached) which indicates there is at least one coordinated water per monomer unit. Heating a solution above 10 °C or adding methanol resulted in decomposition of the polymer. A continuous variation study in solution was not possible since a $p\text{-}CH_3T^-$ to Co^{2+} ratio of seven was required to obtain a clear solution. However, the intrinsic viscosity, spectra and titration results as well as the response of the compound to heat and treatment with methanol all closely parallel the results obtained for the Co^{2+}/T^- system and indicate the two polymers have the same structure.

The data for both Co^{2+} systems are consistent with the monomer units $CoL_2(H_2O)_2$ and $CoL_2(H_2O)(OH)^-$ ($L = T^-$ or $p\text{-}CH_3T^-$). To distinguish between these possibilities, two day old solutions of Co^{2+}/T^-, $Co^{2+}/p\text{-}CH_3T^-$ and, for comparison, Ni^{2+}/T^- polymers were subjected to horizontal slab gel electrophoresis. In all cases the bands moved toward the positive electrode (between 0.8 and 1.2 cm) showing the polymers are negatively charged and indicating the monomer unit for the Co^{2+} polymers is $CoL_2(H_2O)(OH)^-$.

Solutions containing the yellow–orange, polymeric $Ni^{2+}/p\text{-}NO_2T^-$ species have visible spectra with a λ_{max} at 523 nm ($\epsilon = 14$ l mol^{-1} cm^{-1}) which indicates the coordination around the Ni^{2+} ion is octahedral [6b]. Titration of a 0.002 M Ni^{2+}/0.02 M $p\text{-}NO_2T^-$ solution with 0.005 M NaOH gave an equivalence point, at pH 7.8, corresponding to a Ni^{2+} to OH^- ratio of approximately 150 which indicates that water is coordinated only at the ends of the polymer. Electrophoresis of a $Ni^{2+}/p\text{-}NO_2T^-$ solution showed the polymer is negatively charged. Refluxing a solution at 100 °C for several hours was required to decompose the polymer, indicating it is quite stable. Although a continuous variation study in solution was not possible since a $p\text{-}NO_2T^-$ to Ni^{2+} ratio greater than four was needed to obtain a clear solution, the instrinsic viscosity, spectra, electrophoresis and titration results and heat sensitivity data parallel those observed for $(NiT_3^-)_n$ and indicate the polymer has a triple-bridged structure with a monomer unit $Ni(p\text{-}NO_2T)_3^-$. Additional support for this assignment is provided by the fact that an orange solid isolated from the polymer solution analysed as $NaNi(p\text{-}NO_2T)_3 \cdot 5H_2O$.

The 0.001 M Ni^{2+}/0.01 M $p\text{-}CH_3T^-$ solution containing the polymeric, pink–purple $Ni^{2+}/p\text{-}CH_3T^-$ species has a visible spectrum with a λ_{max} at 518 nm ($\epsilon = 25$ l mol^{-1} cm^{-1}). Titration of this solution with 0.005 M NaOH gave an equivalence point, at pH 7.9, corresponding to a Ni^{2+} to OH^- ratio of approximately 100. Electrophoresis of the solution showed the polymer is negatively charged. Heating the solution to 80 °C was required to decompose the polymer. The intrinsic viscosity, spectrum, titration and electrophoresis results and heat sensitivity data parallel those observed for the $(NiT_3^-)_n$ and $[Ni(p\text{-}NO_2T)_3^-]_n$ species and indicate the polymer also has a triple-bridged structure and that the monomer unit is $Ni(p\text{-}CH_3T)_3^-$.

The fact that the intrinsic viscosities of the Co^{2+} polymers, which have two tetrazolate bridges per metal ion, are comparable to the values for the corresponding Fe^{2+} and Ni^{2+} polymers, which have three such bridges per monomer unit, implies that the Co^{2+} species are either as rigid and approximately as long or somewhat less rigid and much longer than the Fe^{2+} or Ni^{2+} species. When viscosity data and a mean molecular weight value (*M*) derived from osmotic pressure measurements on the 0.002 M Co^{2+}/0.02 M T^- solution [2] are fit to the equation $[\eta] = KM^{\alpha}$ with α set equal to the limiting value for rigid rods of 1.8, a K value of 8×10^{-7} ml g^{-1} results. The fact that this value is the same, within experimental error, as that found for the triple-bridged $[NiT_3^-]_n$ provides an indication that the rigidities of the Co^{2+} polymers are comparable to those of the corresponding Fe^{2+} and Ni^{2+} species. The K value is also consistent with values reported for other rigid, rod-like polymers [7].

If the Co^{2+} polymers are as rigid as their Fe^{2+} and Ni^{2+} counterparts, they must also contain a third bridge per monomer unit. Given their stoichiometries, this could only arise from hydrogen bonding between coordinated H_2O and OH^- on adjacent metal ions. The presence of such a bridge, which would be relatively weak, could also explain why the Co^{2+} polymers decompose at much lower temperatures than their triple-tetrazolate-bridged Fe^{2+} and Ni^{2+} counterparts.

The fact that Ni^{2+} forms a polymer with p-NO_2T^- while Fe^{2+} and Co^{2+} do not provides additional support for the proposed minimum electron density requirement. Apparently, even in the presence of the electron-withdrawing p-NO_2 group, the relatively electron-rich d^8 Ni^{2+} supplies enough electron density to the ligand–metal π system to result in soluble polymers.

Since Ni^{2+} forms a soluble polymer with p-CH_3T^-, which contains an electron-donating substituent, it seems likely that the combination of d^9 Cu^{2+} and p-NO_2T^- would also satisfy the electron density requirement for polymer formation. However, no soluble polymer containing Cu^{2+} has been found. The reason may be that strong Jahn–Teller distortion, which is typically present in Cu^{2+} complexes [8], precludes the formation of an effective third bridge.

Triple bridging, which appears to be present in all the soluble polymeric complexes, may accompany the formation of these polymers because only in this configuration is the degree of ligand π^*–metal t_{2g} overlap sufficient to stabilize the soluble polymer relative to the insoluble ML_2 species.

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